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AN

# INTRODUCTION TO THE STUDY
OF THE
# COMPOUNDS OF CARBON;
OR,
# ORGANIC CHEMISTRY.

BY

IRA REMSEN,

PROFESSOR OF CHEMISTRY IN THE JOHNS HOPKINS UNIVERSITY.

London:
MACMILLAN AND CO.,
1885.

---

## PREFACE.

THIS book is intended for those who are beginning the subject. For this reason, special care has been taken to select for treatment such compounds as best serve to make clear the fundamental principles. General relations as illustrated by special cases are discussed rather more fully than is customary in books of the same size; and, on the other hand, the number of compounds taken up is smaller than usual. The author has endeavored to avoid dogmatism, and to lead the student, through a careful study of the facts, to see for himself the reasons for adopting the prevalent views in regard to the structure of the compounds of carbon. Whenever a new formula is presented the reasons for using it are given, so that it may afterward be used intelligently. It is believed that the book is adapted to the needs of all students of chemistry, whether they intend to follow the pure science, or to deal with it in its applications to the arts, medicine, etc. It is difficult to see how, without some such general introductory study, the technical chemist and the student of medicine can comprehend what is usually put before them under the heads of "Applied Organic Chemistry" and "Medical Chemistry."

Without some direct contact with the compounds considered, it is difficult to get a clear idea regarding them and their changes. A course of properly selected experiments, illustrating the methods used in preparing the principal classes of compounds, and the fundamental reactions involved in their transformations, wonderfully facilitates the study. The attempt has been made to give directions for such a course. More than eighty experiments which could be performed in any chemical laboratory are described; and it is hoped that the plan may meet with approval. The time required to perform a fair proportion of these experiments is not great; and the results in the direction of enlarging the student's knowledge of chemical phenomena, will, it is firmly believed, furnish a full compensation for the time spent.

The order in which the topics are taken up will be found to differ somewhat from that commonly adopted. The object in view was, however, not to find a new method, but to find one which would bring out as clearly as possible the beauty and simplicity of the relations which exist between the different classes of carbon compounds. The reasons for the method used are given in the body of the book.

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# CHEMISTRY
# OF THE
# COMPOUNDS OF CARBON.

## CHAPTER I.

## INTRODUCTION.

In studying the compounds of carbon, we cannot fail to be struck by their large number, and by the ease with which they undergo change when subjected to various influences. Mainly on account of the large number, though partly on account of peculiarities in their chemical conduct, it is customary to consider these compounds by themselves. At first, *General Chemistry* was divided into *Inorganic* and *Organic Chemistry*, as it was believed that there were fundamental differences between the compounds included under the two heads. Those compounds which form the mineral portion of the earth were treated under the first head, while those which were found ready formed in the organs of plants or animals were the subject of organic chemistry. It was believed that, as the organic compounds are elaborated under the influence of the life process, there must be something about them which distinguishes them from the inorganic compounds in whose formation the life process has no part. Gradually, however, this idea has been abandoned; for, one by one, the compounds which are found in plants and animals have been made in the chemical laboratory, and without the aid of the life process. The first instance of the preparation of an organic compound by an artificial method was that of urea. This substance was obtained by Wöhler in 1828 from ammonium cyanate. When a water solution of the latter is allowed to evaporate, urea is deposited. Up to the time of Wöhler's discovery, the formation of urea, like that of other organic compounds, was thought to be intimately and necessarily connected with life; but it was thus shown that it could be formed without the intervention of life. Afterward, it was shown that potassium cyanide can be made by passing nitrogen over a heated mixture of carbon and potassium carbonate; and, as potassium cyanate can be made from the cyanide by oxidation, it follows that urea can be made from the elements. Finally, in 1856, Berthelot succeeded in making potassium formate by passing carbon monoxide over heated potassium hydroxide; and in making acetylene, a compound, the composition of which is represented by the formula $C_2H_2$, by passing electric sparks between electrodes of carbon in an atmosphere of hydrogen. Since that time, every year has witnessed the artificial preparation, by purely chemical means, of compounds of carbon which are found in the organs of plants and animals.

It hence appears that the formation of the compounds of carbon is not dependent upon the life process; that they are simply chemical compounds governed by the same laws that govern other chemical compounds; and the name, *Organic Chemistry*, signifying, as it does, that the compounds included under it are necessarily related to organisms, is misleading. Organic chemistry is nothing but the *Chemistry of the Compounds of Carbon*. It is not a science independent of inorganic chemistry, but is just as much a part of chemistry as the chemistry of the compounds of sodium, or of the compounds of silicon, etc.

The name *Chemistry of the Compounds of Carbon* has been objected to as being too broad. Strictly speaking, this title includes the carbonates, and it is customary to treat of these widely distributed substances under the head of Inorganic Chemistry. Most books on Inorganic Chemistry also deal with some of the simpler compounds of carbon, such as the oxides, cyanogen, marsh gas, etc.

This objection is of weight only as far as the carbonates are concerned, and it does not appear strong enough to make the introduction of a new name necessary. It should be mentioned, however, that the name *Chemistry of the Hydrocarbons and their Derivatives* has recently been suggested. The exact significance of this name will appear when the compounds with which we shall have to deal come up for consideration.

**Sources of compounds.** — The compounds of carbon are, for the most part, made in the laboratory; but in preparing them we usually start with a few fundamental compounds which are formed by natural processes. A large number, such as the sugars, starch, cellulose, and the alkaloids, of which morphine, quinine, and nicotine are examples, occur ready formed in plants, but always mixed with other substances. Others, such as urea, uric acid, albumin, etc., occur in animal organisms. *Petroleum*, which has been formed in Nature by processes intimately connected with those which give rise to the formation of coal, contains a large number of compounds consisting of only carbon and hydrogen; and these compounds serve as the starting-points in the preparation of a large number of derivatives. When coal is heated for the purpose of manufacturing illuminating gas, a very complex mixture of liquid and solid products is obtained as a by-product, known as *coal tar*. This substance yields some of the most valued compounds of carbon. A larger number of the compounds of carbon are obtained from this than from any other one source. When bones are heated in the manufacture of bone-black, an oil known as *bone oil* is obtained. Of late, this has proved to be the source of a large number of interesting compounds. In the preparation of charcoal by heating wood, the liquid products are sometimes condensed, and they form the source of several important compounds, among which may be mentioned *wood spirits* or *methyl alcohol*, *acetone*, and pyroligneous or *acetic acid*.

Finally, we are dependent upon the process known as *fermentation* for a number of the most important compounds of carbon. Fermentation, as will be shown, is a general term, signifying any process in which a change in the composition of a body is effected by means of minute animal or vegetable organisms. The best known example of fermentation is that of sugar, which gives rise to the formation of ordinary *alcohol*. Alcohol in turn serves as the starting-point for the preparation of a large number of compounds.

**Purification of the compounds.** — Before the natural compounds of carbon can be studied chemically, they must, of course, be freed from foreign substances; and before the constituents of the complex mixtures, petroleum, coal tar, and bone oil can be studied, they must be separated and purified. The processes of separation and purification are, in many cases, extremely difficult. If the substance is a solid, different methods may be used according to the nature of the substance. *Crystallization* is more frequently made use of than any other process. This is well illustrated, on the large scale, in the refining of sugar, which consists, essentially, in dissolving the sugar in water, filtering through bone-black, which absorbs coloring matter, and then evaporating down to crystallization. When two or more substances are found together, they may, in many cases, be separated by what is called *fractional crystallization*. This consists in evaporating the solution until, on cooling, a comparatively small part of the substance is deposited. This deposit is filtered off, and the solution further evaporated; when a second deposit is obtained, and so on to the end. The successive deposits thus obtained are then recrystallized, each separately, until, finally, the deposits are found to be homogeneous.

The chief solvents used are water, alcohol, ether, benzine, and bisulphide of carbon; alcohol being the most generally applicable.

In the case of liquids, the process of *distillation* is used. The apparatus commonly used is illustrated in Fig. 1.

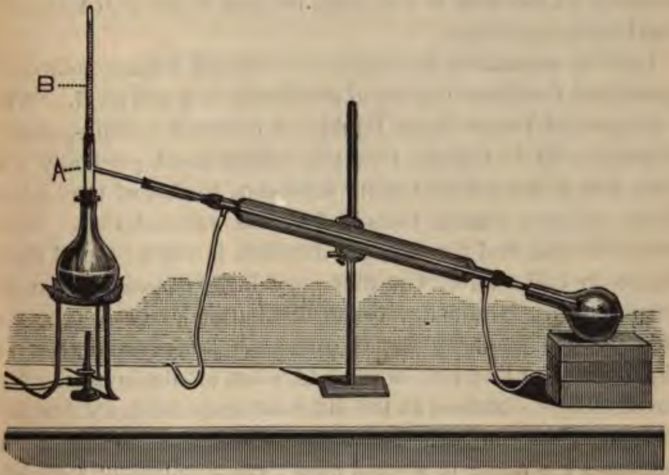


Fig. 1.

The only part of the apparatus which requires explanation is the tube *A*. This is known as the *distilling tube*. It is simply a straight glass tube, about $16^{cm}$ long and 12 to $14^{mm}$ in diameter, to which is attached a smaller branch somewhat inclined downward. The object of the tube is to accommodate a thermometer *B*, which is so fixed by means of a cork, that it is in the centre of the larger tube, and its bulb directly opposite the opening of the smaller branch.

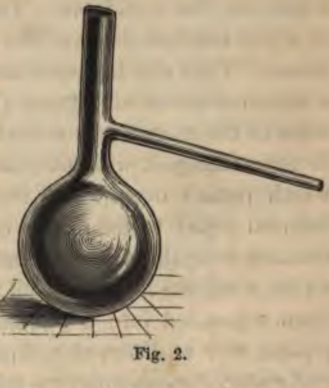


Fig. 2.

For small quantities of liquids, *the distilling flask* is much used. This is a long-necked, round flask, with a branch tube fitted directly into the neck, as shown in Fig. 2. In this apparatus, the thermometer is fitted into the neck of the flask in the same relation to the exit tube as in the larger apparatus.

For the separation of liquids of different boiling-points, the process of *fractional* or *partial distillation* is much used. When a mixture of two or more liquids of different boiling-points is boiled, it will be noticed that the boiling-point gradually rises from that of the lowest boiling substance to that of the highest. Thus, ordinary alcohol boils at 78°, and water at 100°. If the two be mixed, and the mixture distilled, it will be found that it begins to boil at 78°, but that very little passes over at this temperature. Gradually, as the distillation proceeds, the temperature indicated by the thermometer becomes higher and higher, until at last 100° is reached, when all distils over. Now the distillates obtained at the different temperatures differ from each other in composition. Those obtained at the lower temperatures are richer in alcohol than those obtained at the higher temperatures, but none of them contains pure alcohol or pure water. In order to separate the two, therefore, we must proceed as follows: A number of clean, dry flasks are prepared for collecting the distillates. The boiling is begun, and the point at which the first drops of the distillate appear in the receiver is noted. That which passes over while the mercury rises through a certain number of degrees (3, 5, or 10, according to the character of the mixture) is collected in the first flask. The receiver is then changed, without interruption of the boiling, and that which passes over while the mercury rises through another interval equal to the first is collected in the second flask. The receiver is again changed, and a third distillate collected; and so on, until the liquid has all been distilled over. It has thus been separated into a number of fractions, each of which has passed over at different temperatures. In the case of alcohol and water, for example, we might have collected distillates from 78° to 83°, from 83° to 88°, from 88° to 93°, from 93° to 98°, from 98° to 100°. Now a clean distilling flask is taken, and into it introduced the first fraction. This is distilled until the thermometer marks the upper limit of the original first fraction, the new distillate being collected in the flask which contained the first fraction. When this upper limit is reached, the boiling is stopped. It will be found that there is some of the liquid left in the distilling flask. That is to say, assuming that in the first distillation the first fraction was collected between 78° and 83°, on boiling this fraction the second time it will not all come over between these points; when 83° is reached some will be left in the flask. The second fraction is now poured into the distilling flask through a funnel tube, and the boiling is again started. Of the second fraction, a portion will pass over below the point at which it began to boil when first distilled. Collect in the proper flask, and continue the boiling until the thermometer marks the highest point of the fraction last introduced, changing the receiver whenever the indications of the thermometer require it. Now stop the boiling, and pour in fraction No. 3, and so on until all the fractions have been subjected to a second distillation. On examining the new fractions, it will be found that the liquid tends to accumulate in the neighborhood of certain points corresponding to the boiling-points of the constituents of the mixture. The distilling flask is now cleaned, and the whole process repeated. A further separation is thus effected. By continuing the distillation in this way, pure substances may, in most cases, eventually be obtained. That the fractions are pure may be known by the fact that the boiling-points remain constant. In some cases perfect separation cannot be effected by means of fractional distillation; as, for example, in the case of alcohol and water. But still it is valuable, even in such cases, as it enables us to purify the substances, at least partially.

The best examples of distillation carried on on the large scale are those of alcohol and petroleum. Probably the best example *of fractional distillation* is that of the light oil obtained from *coal tar.*

**Experiment 1.** Mix equal parts (about half a litre of each) of alcohol and water. Distil through four or five times, and notice the changes in the quantities obtained in the different fractions.

**Determination of the boiling-point.** — In dealing with liquids, it often is extremely difficult to tell whether they are pure or not. The first and most important physical property which is utilized for this purpose is the boiling temperature, commonly called the *boiling-point*. This is determined by means of an apparatus, such as is described above as used for distilling. The temperature noted on the thermometer when the liquid is boiling is the boiling-point. When great accuracy is required, the point observed directly must be corrected, in consequence of the expansion of the glass and the cooling of that part of the column of mercury which is not in the vapor. Full directions for making these corrections may be found in larger books. A constant boiling-point is characteristic of a pure chemical compound.

**Determination of the melting-point.** — Just as the boiling-point is a very characteristic property of liquid bodies, so the melting-point is an equally characteristic property of many solid bodies. If a substance begins to melt at a certain temperature, and does not melt completely at that temperature, it is, in all probability, impure. By means of the melting-point minute quantities of impurities, which might readily escape detection by other means, are often found. In dealing with the compounds of carbon, determinations of melting-points are very frequently made. In general, only those compounds which have constant melting-points are to be regarded as pure. The determination is made as follows: Small tubes are prepared by heating a piece of ordinary soft glass tubing of $4^{mm}$ to $5^{mm}$ diameter, and drawing it out. If the parts are drawn apart about $12^{cm}$ to $15^{cm}$, two small tubes may be made from the narrowed portion by melting together in the middle, and then *filing off each piece* where it begins to grow wider near the large tube. These small tubes must have thin walls, and be of such internal diameter that an ordinary pin can be introduced into them. A small quantity of the substance to be tested is placed in one of the tubes, enough to make a minute column of about $5^{mm}$ in height. The tube containing the substance is fastened to a thermometer by means of a small rubber band cut from a piece of rubber tubing. The band is placed near the upper part of the tube, and the lower part of the tube, containing the substance, is placed against the bulb of the thermometer. Now a beaker glass of about $100^{cc}$ capacity is filled with pure paraffin, and the latter melted. When it is in liquid condition, the thermometer, with the tube and substance, is introduced into it, and the heating continued with the aid of a small flame until the substance melts. The instant it melts the temperature indicated by the thermometer is noted. This is the *melting-point* required. It is necessary, however, to correct the observed point in the same way as in the case of the boiling-point. Sometimes, instead of paraffin, concentrated sulphuric acid is used in the bath; but, for obvious reasons, the paraffin is to be preferred. For substances which melt below 80°, the temperature at which ordinary paraffin is liquid, water should be used.

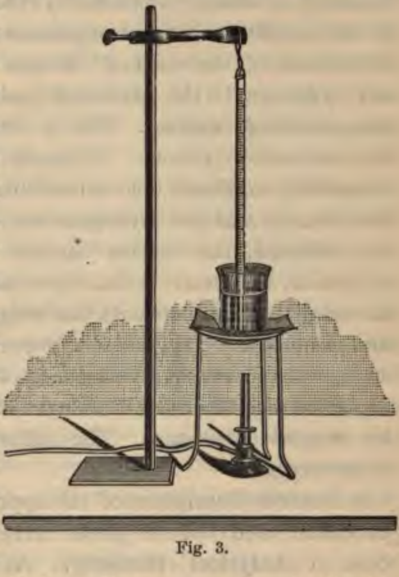


Fig. 3.

**Experiment 2.** Determine the melting-points of a few substances, *such as urea and tartaric acid.* If they do not melt at definite points, *recrystallize them* until they do. Note the melting-points observed, and see how well they agree with those stated in the book. The arrangement of the apparatus above described is shown in Fig. 3. To secure a uniform temperature of the bath, it should be gently stirred with a glass rod during the experiment. The mercury of the thermometer should rise slowly.

**Analysis.** — Having purified the compounds, the next step is to determine their composition. A comparatively small number of the compounds ordinarily met with consist of carbon and hydrogen only; the largest number consist of these two elements together with oxygen; many contain carbon, hydrogen, oxygen, and nitrogen. But, in the derivatives of the fundamental compounds, all other elements may occur. Thus the hydrogen may be partly or wholly displaced by chlorine, bromine, or iodine, as in the so-called substitution-products; and any metal may occur in the salts of the acids of carbon. The estimation of carbon and hydrogen is the principal problem in the analysis of the compounds of carbon. This is effected by what is known as the *combustion process*. A known weight of the substance is completely oxidized, the carbon being thus converted into carbon dioxide, and the hydrogen into water. These two products are collected, the carbon dioxide in a solution of potassium hydroxide, the water in calcium chloride, and weighed. From the weights of the products the weights of carbon and hydrogen are calculated. Oxygen, if present, is not estimated directly, but by difference, *i.e.*, the amounts of carbon and hydrogen found are added together, and the sum subtracted from the weight of the original substance. The difference represents the weight of the oxygen.

A detailed description of the apparatus and of the method of procedure need not be given here, as it can be found in any book on analytical chemistry. A brief description, however, may not be out of place. The combustion is effected in a hard glass tube which is heated by means of a gas furnace constructed for the purpose. Ordinarily, the substance is placed in a narrow porcelain or platinum vessel, called a *boat*, which is duced into the tube with granulated copper oxide. The tube is then connected with (1) a U-tube filled with calcium chloride; (2) a set of bulbs containing a solution of potassium hydroxide, and constructed so as to secure thorough contact of the passing gases with the solution; and (3) a small U-tube filled with solid potassium hydroxide. After the combustion is completed, a current of pure dry oxygen is passed through the tube; and, finally, air is passed until the oxygen is displaced. The method at present used was introduced by Liebig. It has contributed very greatly to a thorough understanding of the compounds of carbon.

Two methods are in common use for the estimation of nitrogen in carbon compounds. The first is known as the *absolute method*. This consists in oxidizing the substance by means of copper oxide; then decomposing, by means of highly-heated metallic copper, any oxides of nitrogen which may have been formed, and collecting the nitrogen. The volume of the nitrogen thus obtained is measured, and its weight easily calculated. The chief difficulty in this method consists in removing the gases contained in the apparatus before the combustion is made. To do this, the simplest way is to use a mercury air-pump. Several simple forms of the pump have been devised for this purpose, and some of them work admirably. Having exhausted all the air, the combustion is made by heating the tube containing the substance and copper oxide and a layer of copper foil; and, finally, the gases are exhausted at the end of the operation. The only three gases which can be present, assuming that the substance contained nothing but carbon, hydrogen, oxygen, and nitrogen, are carbon dioxide, water vapor, and free nitrogen. The water vapor is, of course, condensed, and the carbon dioxide is absorbed by passing the gases through a solution of potassium hydroxide, leaving the nitrogen thus alone.

The second method for the estimation of nitrogen consists in heating the substance with a mixture of sodium hydroxide and quicklime, called *soda-lime*. The nitrogen is thus converted into ammonia, which is collected in a known quantity of dilute hydrochloric or sulphuric acid. After the operation, the amount of acid remaining unneutralized is determined by titration ; and from this the amount of ammonia formed can be calculated; and from this, in turn, the amount of nitrogen. This method is not applicable to all compounds, because the nitrogen of some compounds is not converted into ammonia under the circumstances mentioned.

As regards the estimation of other constituents of carbon compounds, it need only be said that in most cases it is necessary to get rid of the carbon and hydrogen by some oxidizing process before the estimation can be made. Thus, in estimating sulphur, it is common to fuse the substance with potassium nitrate and hydroxide, when the carbon and hydrogen are oxidized, and the sulphur is left in the form of potassium sulphate, and may be estimated in the usual way.

**Formula.** — The deduction of the formula of a compound from the results of the analysis involves two steps. The first is a matter of simple calculation. It is assumed that the students who use this book are already familiar with the method of calculating the formula from the analytical results ; but an example will, nevertheless, be given. Suppose that the analysis has shown that the substance contains 52.18 per cent carbon, 13.04 per cent hydrogen, and 34.78 per cent oxygen. To get the atomic proportions, divide the figures representing the percentages of the elements by the corresponding atomic weights. We have thus : —

| | Per Centage. | | At. Wt. | | Proportionate No. of Atoms. | | |
|---|---|---|---|---|---|---|---|
| C | 52.18 | ÷ | 12 | = | 4.35 | – | 2 |
| H | 13.04 | ÷ | 1 | = | 13.04 | – | 6 |
| O | 34.78 | ÷ | 16 | = | 2.17 | – | 1 |

That is to say, accepting the atomic weights, 12 for carbon and 16 for oxygen, the simplest figures representing the number of *atoms of the* three elements in the compound are 2 for carbon, 6 for hydrogen, and 1 for oxygen. According to this, the simplest formula which can be assigned to a substance giving the above results on analysis is $C_2H_6O$. But the formula $C_4H_{12}O_2$ is equally in accordance with the analytical results, and we can only decide between the two by determining the *molecular weight.* This, as is known, is done by determining the specific gravity of the substance in the form of vapor. This operation is of the greatest importance. It is assumed that the student, who has already studied the elements of inorganic chemistry, is familiar with it, and with the exact connection which exists between it and the molecular weights of compounds. A few statements in regard to the connection will, however, be made here, in order to recall its chief points, and to impress upon the mind of the student its fundamental importance.

Every chemical formula is intended to represent the molecule of a compound and the composition of the molecule. Our conception of the molecule is based almost exclusively on Avogadro's hypothesis, according to which equal volumes of all gases contain the same number of molecules. Hence, by comparing equal volumes of bodies in the form of gas or vapor, we get figures which bear to each other the same relations as the weights of the molecules. The figures called *the specific gravities* express the relations between the weights of equal volumes. In the case of gases, air is taken as the standard, and the weights of other gases are compared with this standard. Thus, if we say that the specific gravity of a gas is 0.918, we mean that if we call the weight of any volume of air 1, that of the same volume of the other gas measured under the same conditions of temperature and pressure is 0.918. If we assign to any compound a certain molecular weight, the molecular weights of other gaseous compounds can be determined without difficulty. We must, therefore, first select some substance, the molecule of which may be used as the standard. Hydrochloric acid is commonly taken, because hydrogen and chlorine unite with *each other in only* one proportion, and there is good evidence in favor of the view that it represents the simplest kind of combination, viz., that of one atom of one element with one of another. Hydrogen and chlorine are present in the compound in the proportion of 1 part of hydrogen to 35.4 parts of chlorine: hence the simplest molecular weight which can be assigned to the compound, the atomic weight of hydrogen being 1, is 36.4. The molecular weight of this standard molecule is, therefore, taken to be 36.4, and we have now simply to compare the weights of other gases with that of hydrochloric acid in order to know their molecular weights. Thus, to illustrate by means of the body whose atomic relations we found by analysis to be represented by the formulas $C_2H_6O$, $C_4H_{12}O_2$, etc., if this body be converted into vapor and its specific gravity determined, it might be found to be 1.6. The relation between the molecular weight of any body and its specific gravity is expressed by the equation

$$M = d \times 28.88,$$

in which $M$ is the molecular weight, and $d$ the specific gravity of the substance in the form of gas or vapor. As $d$ is 1.6 in the case under consideration, we have

$$M\,(\text{the unknown molecular weight}) = 1.6 \times 28.88 = 46.2.$$

If the formula of the compound is $C_2H_6O$, the molecular weight, being the sum of the weights of the constituent atoms, is

$$2 \times 12 + 6 \times 1 + 16 = 46,$$

which agrees with the figure deduced from the specific gravity. It therefore follows that the formula $C_2H_6O$ is correct.

There are some other methods which may be used in determining the molecular weight of a compound. Among these may be mentioned the analysis of salts. To illustrate this, take the case of acetic acid. Analysis shows us that it must be represented by one of the formulas $CH_2O$, $C_2H_4O_2$, $C_3H_6O_3$, etc. If we make the silver salt, we find that its analysis leads us to formula $C_2H_3O_2Ag$, and not $CHOAg$, and we hence conclude olecular formula of acetic acid is $C_2H_4O_2$.

The methods for determining the specific gravity of vapors are assumed to have been described in the course in inorganic chemistry, which the student should have followed before beginning the study of the compounds of carbon.

**Structural formula.** — The formulas $C_2H_6O$, $C_2H_4O_2$, $C_3H_8$, etc., tell us simply the composition of the three bodies represented, and tell us also the relative weights of their molecules. In studying the chemical conduct of these bodies, their decomposition, and the modes of preparing them, we become familiar with many facts which it is desirable to represent by means of the formulas. Thus, for example, but one of the four parts of hydrogen represented in the formula of acetic acid, $C_2H_4O_2$, can be replaced by metals. It plainly differs from the three remaining parts, and it is natural to conclude that it is held in the molecule in some way differently from the other three. We may, therefore, write the formula $C_2H_3O_2.H$, which is intended to call attention to the difference. By further study of acetic acid, we find that that particular hydrogen, which gives to it its acid properties, and which, in the above formula, is written by itself, is intimately associated with oxygen. It may be removed with oxygen by very simple reactions, and the place of both taken by one atom of some other element; as, for example, chlorine. Thus, when acetic acid is treated with phosphorus trichloride, $PCl_3$, it is converted into acetyl chloride, $C_2H_3OCl$, according to this equation: —

$$3\ C_2H_4O_2 + PCl_3 = 3\ C_2H_3OCl + PO_3H_3.$$

The result of the action is the direct replacement of one atom of hydrogen and one atom of oxygen in acetic acid by one atom of chlorine, a fact which certainly points to an intimate connection between the hydrogen and oxygen in the acid. Further, when acetyl chloride is brought in contact with water, acetic acid is regenerated, hydrogen and oxygen from the water entering into the place occupied by the chlorine, as represented in this equation: —

$$C_2H_3OCl + H_2O = C_2H_4O_2 + HCl.$$

From facts of this kind the conclusion is drawn that in acetic acid hydrogen and oxygen are *connected;* or, as it is said, *linked together;* and this conclusion is represented in chemical language by the formula $C_2H_3O.OH$, which may serve as a simple illustration of what are called *structural* or *constitutional* formulas. In all compounds the attempt is made, by means of a thorough study of their chemical conduct, to trace out the connections existing between the constituent atoms. When this can be done for all the atoms contained in a molecule, the *structure* or *constitution* of the molecule or of the compound is said to be determined. The structural formulas which have been determined by proper methods have proved of much value in dealing with chemical reactions, as they enable the chemist who *understands* the language in which they are written to see relations which might easily escape his attention without their aid. In order to *understand* them, however, the student must have a knowledge of the reactions upon which they are based; and he is warned not to accept any chemical formula unless he can see the reasons for accepting it. He should accustom himself to ask the question, *upon what facts is it based?* whenever a formula is presented for the first time. If he does this conscientiously he will soon be able to use the language intelligently, and the beauty of the relations which exist between the large number of compounds of carbon will be revealed to him. If he does not, his mind will soon be in a hopeless muddle, and what he learns will be of little value to him. For the beginner, this piece of advice is of vital importance: *Study with great care the reactions of compounds; study the methods of making them, and the decompositions which they undergo. The formulas are but the condensed expressions of the conclusions which are drawn from the reactions.*

**General principle of classification of the compounds of carbon.** — In considering the elements and compounds included under the head of Inorganic Chemistry, the fundamental substances are, of course, the elements. The properties of the elements enable us to separate them, for study, into a number of groups; as, for example, the chlorine group, including bromine, iodine, and fluorine; the oxygen group, in which are included sulphur, selenium, and tellurium. To recall the method generally adopted, we may take the chlorine group. In studying the members of this group, there is found great similarity in their properties. Their hydrogen compounds next present themselves, and here the same similarity is met with. Then, in turn, the oxygen and the oxygen and hydrogen compounds are considered, and again the resemblances in properties between the corresponding compounds of chlorine, bromine, and iodine are met with. We thus have groups of elements, and of the derivatives of these elements: as, —

| | | |
|---|---|---|
| Cl | ClH | $ClO_3H$ |
| Br | BrH | $BrO_3H$ |
| I | IH | $IO_3H$, etc. |

Of course, the chlorine group is quite distinct from the oxygen group and from all other groups; and each member of the chlorine group is, at least so far as we know, quite independent of the other members. We cannot make a bromine compound from a chlorine compound, or a chlorine compound from a bromine compound without directly replacing the one element by the other.

Now, when we come to study the compounds of carbon, we shall find that the same general principle of classification is made use of; only, in consequence of the peculiarities of the compounds, the system can be carried out much more perfectly; the members of the same group can be transformed one into the other, and it is also in our power to pass from one group to another by means of comparatively simple reactions.

The simplest compounds of carbon are those which contain only hydrogen and carbon, or the *hydrocarbons*. All the other compounds may be regarded as derivatives of the hydrocarbons.

To begin with, there are several groups or series of hydrocarbons, which correspond somewhat to the different groups of elements. The members of one and the same series of hydrocarbons resemble each other more closely than the members of one and the same series of elements. Although we have indications of the existence of more than ten series of these hydrocarbons, only three or four of the series are at all well known, and of these, but two include more than two or three members which will need to be considered in this book.

Starting with any series of hydrocarbons, several classes of derivatives may be obtained by treating the fundamental compounds with different reagents. The chief classes of these derivatives are: (1) those containing halogens; (2) those containing oxygen, among which are the acids, alcohols, ethers, etc.; (3) those containing sulphur; and (4) those containing nitrogen. Corresponding to every hydrocarbon, then, we may expect to find representatives of these different classes of derivatives. But the relations existing between any hydrocarbon and its derivatives are the same as those existing between any other hydrocarbon and its derivatives. Hence, if we *know* what derivatives one hydrocarbon can yield, we know what derivatives we may expect to find in the case of every other hydrocarbon. The student who, for the first time, undertakes the study of carbon chemistry, is very apt to feel overwhelmed by the enormous number of compounds described in the book or by the lecturer. This large number is really not a serious matter. No one is expected to become acquainted with every compound. A great many of these need only be referred to for the purpose of indicating the extent to which the series to which they belong have been developed. In general, the members of any series so closely resemble one another, that, if we understand the simpler members, we have a fair knowledge of the more complicated members.

It is proposed, in this treatise, to consider only the more *important compounds* and the more important reactions, the object being rather to give a clear, general notion of the subject, than detailed information regarding particular compounds. Should the student desire more specific information concerning the properties of any of the compounds mentioned, he can easily find it in some larger book. It will, however, hardly be profitable for him, at the outset, to burden his mind with details. He may thereby sacrifice the general view, which it is so important that he should gain as quickly as possible.

The plan which will be followed is briefly this: Of the first series of hydrocarbons *two* members will be considered. Then the derivatives of these two will be taken up. These derivatives will serve admirably as representatives of the corresponding derivatives of other hydrocarbons of the same series, and of other series. Their characteristics, and their relations to the hydrocarbons will be dwelt upon, as well as their relations to each other. Thus, by a comparatively close study of two hydrocarbons and their derivatives, we may acquire a knowledge of the principal classes of the compounds of carbon. After these typical derivatives have been considered, the entire series of hydrocarbons will be taken up *briefly*, only such facts being dealt with at all fully as are not illustrated by the first two members.

After the first series has been studied in this way, and a clear idea of the relations between the various classes has been obtained, a second series will be taken up and treated in a similar way, and so on. But, as already stated, but few of the series require very much attention at the beginning. The first series which will be used for the purpose of illustrating the general principles is one of the *two* most important series, and of the only two that need be considered at all fully at present.

# CHAPTER II.

## METHANE AND ETHANE.—HOMOLOGOUS SERIES.

If we were to study all the hydrocarbons known, and were then to arrange them in groups according to their properties, we would find that a large number of them resemble *marsh gas* in their general conduct. Some of the points of resemblance are these: They are very stable, resisting with marked power the action of most reagents; and nothing can be added to them directly,—if any change takes place in them, hydrogen is first given up. On arranging these substances according to the number of carbon atoms contained in them, we have a remarkable series, the first six members of which, together with their formulas, are included in the subjoined table:—

| | |
|---|---|
| Methane (or Marsh Gas) | $CH_4$. |
| Ethane | $C_2H_6$. |
| Propane | $C_3H_8$. |
| Butane | $C_4H_{10}$. |
| Pentane | $C_5H_{12}$. |
| Hexane | $C_6H_{14}$. |

On examining the formulas given, we see that the difference in composition between any two consecutive members is represented by $CH_2$. Thus, adding $CH_2$ to marsh gas, $CH_4$, we get ethane, $C_2H_6$; adding $CH_2$ to $C_2H_6$, we get $C_3H_8$, and so on, in each successive step. Any series of this kind, in which the successive members increase in complexity by $CH_2$, is called a *homologous series*.

Just as the members of a homologous series of hydrocarbons differ from one another by $CH_2$, or some multiple of it, so also the members of any class of derivatives of these hydrocarbons differ from each other in the same way, and form homologous series. Thus, running parallel to the hydrocarbons mentioned above, we have two homologous series of oxygen derivatives, as indicated below:—

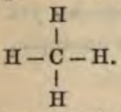
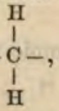
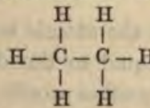
$$CH_4 - CH_4O - CH_2O_2.$$
$$C_2H_6 - C_2H_6O - C_2H_4O_2.$$
$$C_3H_8 - C_3H_8O - C_3H_6O_2.$$
$$C_4H_{10} - C_4H_{10}O - C_4H_8O_2.$$
$$C_5H_{12} - C_5H_{12}O - C_5H_{10}O_2.$$
$$C_6H_{14} - C_6H_{14}O - C_6H_{12}O_2.$$

The relation observed between the members of the homologous series mentioned is by no means a peculiarity of the marsh gas series of hydrocarbons and of their derivatives, but is observed in connection with all other series of hydrocarbons and their derivatives.

Strictly speaking, there is perhaps no analogy for this remarkable fact among the elements and their compounds, yet facts which suggest analogy are known. Consider, for example, the chlorine series. We have

Chlorine, with the atomic weight, 35.4
Bromine, " " " 80.
Iodine, " " " 127.

As is well known, the difference between the atomic weights of chlorine and bromine is approximately equal to the difference between those of bromine and iodine. In other words, there is a regular increase in complexity as we pass from chlorine to iodine. Or, at least, there is a regular increase in the atomic weights of these similar elements, just as there is a regular increase in the molecular weights of the similar members of a homologous series. While, however, a satisfactory hypothesis has been offered to account for the latter fact, and experimental evidence is strongly in favor of the hypothesis, no satisfactory explanation of the former has been offered; or rather no satisfactory experimental evidence has been furnished in favor of the various hypotheses which from time to time have been put forward to account for the similarity between members of the same group of elements.

The view at present held in regard to the nature of homology is founded, primarily, upon the idea that carbon is quadrivalent. If carbon is quadrivalent, it will readily be seen that the compound, marsh gas, $CH_4$, is saturated; that is, the molecule cannot take up anything without losing hydrogen. In order, therefore, that we may get a compound containing two atoms of carbon in the molecule, some of the hydrogen must first be given up. With our present views, we cannot conceive of union taking place directly between the molecules $CH_4$ and $CH_4$, but we can conceive of union taking place between the molecules $CH_3$ and $CH_3$, to form a molecule $C_2H_6$, which in turn is saturated. Representing graphically what is believed to take place, we have, first, marsh gas, which we may represent thus,  $\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$. If this loses one atom of hydrogen, we have the unsaturated molecule  $\begin{array}{c} H \\ | \\ H-C- \\ | \\ H \end{array}$, which is capable of uniting with another molecule of the same kind to form the more complex molecule  $\begin{array}{c} H\ \ H \\ |\ \ \ | \\ H-C-C-H \\ |\ \ \ | \\ H\ \ H \end{array}$, or $C_2H_6$, which is believed to express the relation existing between marsh gas, $CH_4$, and ethane, $C_2H_6$, or between any two adjoining members of a homologous series. The evidence in favor of this view will be presented when the reactions are considered by means of which the hydrocarbons are made. The explanation offered, and now generally accepted, involves the idea that carbon atoms have the power of uniting with each other. And, as the explanation for the relation between the first and second members is, in principle, the same as for the relation between the second and third, the third and fourth, etc., it follows that this power of carbon atoms to unite with each other is very extensive. It is to the power which carbon possesses of forming homologous series, or to the power of the atoms of carbon to unite with each other, that we owe the large number of compounds of this element.

**Methane (marsh gas, fire damp), $CH_4$.** — This hydrocarbon is found rising from pools of stagnant water in marshy districts. If a bottle be filled with water and inverted with a funnel in its neck in such a pool, some of the gas may be collected by holding the funnel over the bubbles rising from the bottom. It is also found in large quantities mixed with air, in coal mines, and sometimes issues from the earth, in company with other gases, in the neighborhood of petroleum wells.

It may be prepared by passing a mixture of carbon bisulphide and hydrogen sulphide or water vapor over ignited metals, as indicated in the following equations: —

$$CS_2 + 2\,H_2S + 8\,Cu = CH_4 + 4\,Cu_2S,$$

and $$CS_2 + 2\,H_2O + 6\,Cu = CH_4 + 2\,Cu_2S + 2\,CuO.$$

These methods are of special interest for the reason that they indicate the possibility of making marsh gas from the elements; carbon bisulphide, hydrogen sulphide, and water all being made readily from the elements.

It is formed, as its occurrence in marshes indicates, by the decomposition of organic matter under water. In pure condition it is made most readily by mixing 2 parts sodium acetate, 2 parts potassium hydroxide, and 3 parts quicklime, and heating the mixture. Writing sodium instead of potassium hydroxide, the action which takes place is represented thus: —

$$NaC_2H_3O_2 + NaOH = CH_4 + Na_2CO_3.$$

It will be shown hereafter that most acids of carbon break up in a similar way, yielding a hydrocarbon and a carbonate.

*Properties.* Marsh gas is colorless and inodorous. It is slightly soluble in water, but not so much so as to prevent its collection over water. It burns. Its mixture with air is explosive. It is this mixture which is the cause of the explosions which so frequently take place in coal mines.

***Experiment 3.*** Make marsh gas from sodium acetate. Collect over water. Burn some as it escapes from a jet. Mix a little with seven to eight times its volume of air in a wide-mouthed cylinder of not more than 150 to 200$^{cc}$ capacity. Explode by applying a lighted taper.

*Reagents*, in general, do not act readily upon marsh gas. *Chlorine* in diffused daylight gradually replaces the hydrogen, forming a series of compounds which will be considered under the head of the halogen derivatives of methane. The simplest of them has the composition represented by the formula $CH_3Cl$, and is known as *chlor-methane* or *methyl chloride*.

**Ethane, $C_2H_6$.** — Ethane rises from the earth from some of the gas wells in the regions in which petroleum occurs. It is also found dissolved in crude petroleum.

It can be made from methane by introducing a halogen and making a compound like chlor-methane, $CH_3Cl$. As the corresponding iodine derivative is less volatile, it is used. This iodo-methane, $CH_3I$, is treated with zinc or sodium in some neutral medium, as, for example, anhydrous ether. The reaction which takes place is represented thus: —

$$CH_3I + CH_3I + 2\ Na = C_2H_6 + 2\ NaI.$$

This method of building up more complex from simpler hydrocarbons has been used extensively; and it is well calculated to show the relations between the substances formed and the simpler ones from which they are made.

*An operation* of the kind involved in the above-mentioned preparation of ethane is called a *synthesis*. The essential feature of the synthesis is the formation of a more complex body from simpler ones. Our knowledge of the structure of the compounds of carbon is largely dependent upon the use of various methods of synthesis. For example, in the case under consideration, the synthesis gives us at once a clear view of the relations between ethane and methane, and also suggests that homology may be due to similar relations between the successive members of the series,—a view which is fully confirmed by the synthetical preparation of the higher members. A similar method of synthesis has been used in the preparation of tetrathionic acid from sodium thiosulphate. The action is represented thus:—

$$\underset{\substack{\text{Two mol. sodium}\\ \text{thiosulphate.}}}{\left.\begin{array}{l}Na_2S_2O_3\\ Na_2S_2O_3\end{array}\right\}} + I_2 = \underset{\substack{\text{Sodium tetra-}\\ \text{thionate.}}}{\begin{array}{l}NaS_2O_3\\ NaS_2O_3\end{array}} > + \ 2\ NaI.$$

# CHAPTER III.

## HALOGEN DERIVATIVES OF METHANE AND ETHANE.

**Substitution.** — When methane and chlorine are brought together in diffused daylight, action takes place gradually; hydrochloric acid gas is given off, and one or more products are obtained, according to the length of time the action continues. The products have been studied carefully, and four have been isolated. The composition of these products is represented by the formulas $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$, and $CCl_4$. We see thus that the action of chlorine consists in replacing, step by step, the hydrogen of the hydrocarbon. The action is represented by the four equations: —

$$\begin{array}{lllllll}
(1) & CH_4 & + Cl_2 & = & CH_3Cl & + HCl; \\
(2) & CH_3Cl & + Cl_2 & = & CH_2Cl_2 & + HCl; \\
(3) & CH_2Cl_2 & + Cl_2 & = & CHCl_3 & + HCl; \\
(4) & CHCl_3 & + Cl_2 & = & CCl_4 & + HCl.
\end{array}$$

This replacement of hydrogen by chlorine is an example of what is known as *substitution*. We shall find that most hydrocarbons are very susceptible to the influence of the halogens and a number of other reagents, such as nitric acid, sulphuric acid, etc., and that thus a large number of derivatives may be made, differing from the hydrocarbons in that they contain one or more halogen atoms or complex groups in the place of the same number of hydrogen atoms. It must be borne in mind that the mere fact that chlorine, in acting upon marsh gas, *replaces an equivalent* quantity of hydrogen, does not prove that the chlorine in the product occupies the same place that the replaced hydrogen did. Nevertheless, a careful study of all the facts regarding the products thus formed has led to the belief that the substituting atom or residue does occupy the same place, or bear the same relation to the carbon atom as the hydrogen did.

The name *substitution-products* properly includes all products made from the hydrocarbons, or from other carbon compounds, by the substitution process. The principal ones are those formed by the action of the halogens, or the *halogen substitution-products;* those formed by the action of nitric acid, or the *nitro-substitution-products;* and those formed by the action of sulphuric acid, or the *sulphonic acids.* The last are, however, not commonly spoken of as substitution-products.

**Chlor-methane, methyl chloride, $CH_3Cl$.**
**Brom-methane, methyl bromide, $CH_3Br$.**
**Iodo-methane, methyl iodide, $CH_3I$.**

The chlorine and bromine products can be made by treating methane with the corresponding element. They can be most easily made by treating methyl alcohol with the corresponding hydrogen acids: —

$$\underset{\text{Methyl alcohol.}}{CH_4O} + HCl = \underset{\text{Chlor-methane.}}{CH_3Cl} + H_2O.$$

**Di-iodo-methane, methylene iodide, $CH_2I_2$.** — This substance is the principal halogen derivative of methane containing two halogen atoms. It is made from iodoform or tri-iodo-methane, $CHI_3$, by treating with hydriodic acid, which latter acts simply as a reducing agent: —

$$CHI_3 + H_2 = CH_2I_2 + IH.$$

As will be seen, this is a case of *reverse substitution;* in other words, the action is the opposite of that described above as substitution. Methylene iodide is a liquid which boils at 180°, *and has the* specific gravity 3.342.

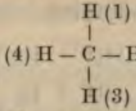
**Chloroform, $CHCl_3$.** } **Bromoform, $CHBr_3$.** } **Iodoform, $CHI_3$.** } The best known and most extensively used of these three derivatives is *chloroform* or tri-chlor-methane. It is made by treating ordinary alcohol with "bleaching powder." The action is deep-seated, involving at least three different stages. It will be referred to more fully under the head of chloral (which see). Chloroform is a heavy liquid of specific gravity 1.526. It has an ethereal odor, and a somewhat sweet taste. It is scarcely soluble in water. It boils at 62°. It is one of the most valuable anæsthetics, though there is some danger attending its use.

**Experiment 4.** Mix $430^g$ good bleaching powder and 1½ litres water in a good sized flask. Add $100^{cc}$ alcohol (88 to 89 per cent), and $100^g$ quicklime, and distil in a water bath. A mixture of alcohol, water, and chloroform collects in the receiver. Add milk of lime and calcium chloride. Remove the chloroform by means of a pipette.

*Iodoform*, which is used quite extensively in surgery, is made by bringing together alcohol, an alkali, and iodine. It is a solid substance, soluble in alcohol and ether, but insoluble in water. It crystallizes in delicate, six-sided, yellow plates. Melting-point, 119°.

**Experiment 5.** Dissolve $20^g$ crystallized sodium carbonate in $100^g$ water. Pour $10^g$ alcohol into the solution, and, after heating to 60° to 80°, add gradually $10^g$ iodine. The iodoform separates from the solution.

*Tetra-chlor-methane*, $CCl_4$, is made by treating carbon bisulphide with chlorine, and by treating chloroform with iodine chloride, $ICl$.

*Equivalence of the hydrogen atoms in methane.* Having thus seen that the hydrogen atoms of methane can easily be replaced, an interesting question suggests itself as to whether these hydrogen atoms all bear the same relation to the carbon atom. We *accept the conclusion* that the carbon atom is quadrivalent, and that each of the four hydrogen atoms is in combination with it, as indicated in the formula  $$\begin{array}{c} \mathrm{H}\,(1) \\ | \\ (4)\,\mathrm{H} - \mathrm{C} - \mathrm{H}\,(2) \\ | \\ \mathrm{H}\,(3) \end{array}$$ Do the atoms numbered 1, 2, 3, and 4 bear the same relation to the carbon or not? If they do not, then, on replacing H (1) by chlorine, the product should be different from that obtained by replacing H (2), H (3), or H (4); or, it should be possible to make more than one variety of chlor-methane and of similar products. This subject is an extremely difficult one to deal with. We can only say that, although chlor-methane has been made in several ways, the product obtained is always the same one; and the same is true of all other substitution-products of methane. *Hence, we have no reason whatever for believing that there are any differences between the hydrogen atoms of methane. We therefore conclude that they all bear the same relation to the carbon atom.*

This conclusion is of fundamental importance in dealing with the higher members of the methane series, and, indeed, in dealing with all carbon compounds, as will be seen later.

**Chlor-ethane, ethyl chloride, $C_2H_5Cl$.**
**Brom-ethane, ethyl bromide, $C_2H_5Br$.**
**Iodo-ethane, ethyl iodide, $C_2H_5I$.**

These substances are all liquids having pleasant ethereal odors. The first boils at 12°, the second at 38.8°, and the third at 72°. They are most readily made from alcohol, by treating with the corresponding hydrogen acids. In the case of the bromide and iodide, it is simpler to treat the alcohol with red phosphorus and the halogen. The action is similar to that involved in making hydrobromic acid by treating water with red phosphorus and bromine. It will be shown that alcohol is a hydroxide, in which hydroxyl (OH) is in combination with the group $C_2H_5$, *called ethyl*, as represented in the formula $C_2H_5.OH$. When bromine is brought in contact with red phosphorus, the tribromide, $PBr_3$, is formed, and this acts upon the alcohol thus : —

$$\left.\begin{array}{l} C_2H_5.OH \quad\;\; Br \\ C_2H_5.OH + Br \\ C_2H_5.OH \quad\;\; Br \end{array}\right\} P = 3\ C_2H_5Br + P(OH)_3.$$

When water is used instead of alcohol, the bromine appears in combination with hydrogen as hydrobromic acid.

**Experiment 6.** Arrange an apparatus as represented in Fig. 4.

In the flask place $10^{g}$ red phosphorus and $60^{g}$ absolute alcohol. Put $60^{g}$ bromine in the glass-stoppered funnel, and, by means of the stopcock, let the bromine enter the flask very slowly, drop by drop. After allowing the mixture to stand for two or three hours, gently heat the water-bath, and the brom-ethane will distil over. Place the distillate in a glass-stoppered cylinder, and shake it first with water to which some caustic soda has been added, and then two or three times with water alone. Separate the water from the brom-ethane either by means of a pipette[1] or a separating funnel. Add two or three pieces of fused

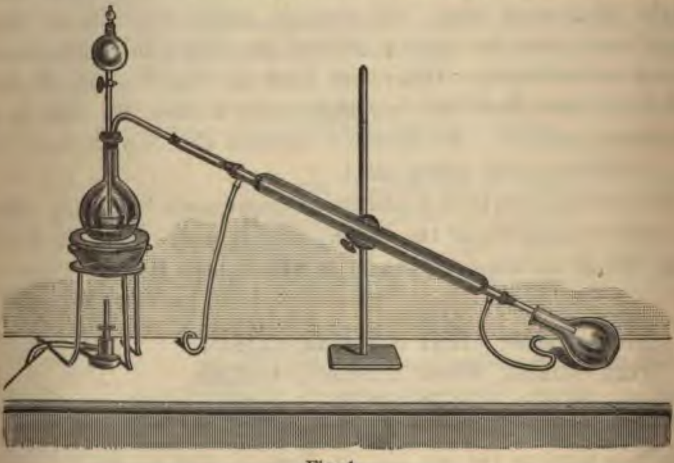


Fig. 4.

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[1] A good pipette for separating two liquids of different specific gravities may be easily follows: Select a piece of glass tubing about 1.5 to $2^{cm}$ internal diameter, and a

calcium chloride the size of a small marble, and let stand for a few hours. Then pour off into a clean, dry distilling bulb, and distil, noting the boiling-point.

Among the many halogen substitution-products of ethane containing more than one halogen atom, only two will be mentioned. These are the two *di-chlor-ethanes*, both of which are represented by the formula $C_2H_4Cl_2$. The existence of these two substances, having the same composition but entirely different properties, affords a good example of what is known as *isomerism.*

**Isomerism.** — One of the most striking and interesting facts with which we become familiar in studying carbon compounds, is the frequent occurrence of two, and often more, substances containing the same elements in the same proportions by weight. Bodies which bear this relation to each other are said to be *isomeric.*

*Isomerism* is of two kinds: (1) Bodies may have the same per centage composition and the same molecular weights. Such bodies are said to be *metameric*. The di-chlor-ethanes, $C_2H_4Cl_2$, for example, are metameric. (2) Bodies which have the same per centage composition but different molecular weights are said to be *polymeric*. Acetylene, $C_2H_2$, benzene, $C_6H_6$, and styrene, $C_8H_8$, are polymeric.

second that will fit snugly into it, so that it can be moved up and down without difficulty. Draw out the larger tube, and fit to it a tube of about $6^{mm}$ diameter and $16^{cm}$ long. Then draw out this last tube to a small opening. Close the smaller of the two large tubes by melting it together. Finally, put this tube into the largest one, and draw over the two a broad piece of thick rubber tubing, which will close the opening between the two, and at the same time permit the upward and downward movement of the smaller tube. The pipette has the form represented in Fig. 5.

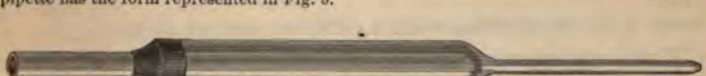
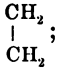


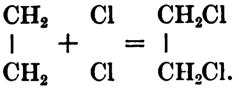
Fig. 5.

The dimensions may be varied, but the following will be found convenient: length of widest tube about 16 to $20^{cm}$; total length of inner tube, or piston, about 25 to $30^{cm}$. Instead of drawing the large tube out and fitting the smaller tube to it, the union may be made by means of a cork.

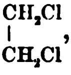
The cause of isomerism is undoubtedly to be found in the different relations which the parts of isomeric compounds bear to each other. Our structural formulas, which show the relations between the parts of compounds which have been traced out by a study of the chemical conduct of these compounds, give us an insight into the causes of isomerism. To illustrate, let us take the two di-chlor-ethanes. One of these is made by treating ethane, the other by treating ethylene, $C_2H_4$, with chlorine. In the first case the action is substitution; in the second, the chlorine is added directly to ethylene, thus, —

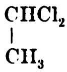
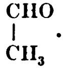
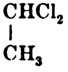
$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$

The product from ethylene is called *ethylene chloride;* that from ethane, *ethylidene chloride.* It will be shown that ethylene is to be represented by the formula  $\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}$; that is, that in it two hydrogen atoms are in combination with each of the carbon atoms. Now, if chlorine is brought in contact with this substance, we would naturally expect each of the carbon atoms to take up one atom of chlorine, and thus to become saturated, as represented in the equation, —



$$\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array} + \begin{array}{c} Cl \\ \\ Cl \end{array} = \begin{array}{c} CH_2Cl \\ | \\ CH_2Cl. \end{array}$$

Chlorine is taken up, and it is believed that the ethylene chloride obtained has the structure represented in the formula  $\begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}$, the distinctive feature of which is that each of the chlorine atoms is in combination with a different carbon atom.

We, however, can conceive of another possibility; viz., that the chlorine atoms are both in combination with the same carbon atom, as represented in the formula  $\begin{array}{c} CHCl_2 \\ | \\ CH_3 \end{array}$, and we would be inclined to the view that this represents the structure of ethylidene chloride. Fortunately we have experimental evidence to support this view. It will be shown that aldehyde has the formula  $\begin{matrix} CHO \\ | \\ CH_3 \end{matrix}$. When aldehyde is treated with phosphorus pentachloride, two chlorine atoms take the place of the oxygen. A product which must be represented by the formula  $\begin{matrix} CHCl_2 \\ | \\ CH_3 \end{matrix}$ is formed, and this is identical with ethylidene chloride. Thus it will be seen that the difference between the two isomeric compounds, ethylene chloride and ethylidene chloride, may be said to depend upon the fact that in the former the two chlorine atoms are in combination with different carbon atoms, while in the latter both are in combination with the same carbon atom.

*General characteristics of the halogen derivatives of methane and ethane.* The one characteristic to which it is desirable that special attention should be called is the firmness with which the halogens are held in the compounds. Chlorine, in combination with a metal in the form of a soluble compound, can always be removed by addition of silver nitrate. It cannot easily be so removed when present in substitution products of the hydrocarbons. If silver nitrate be added to a solution of chlor-methane, $CH_3Cl$, no precipitate is formed. On the other hand, when chlor-methane is heated with a silver compound, the chlorine is removed. Sodium and zinc have the power of extracting the chlorine, bromine, etc., from halogen derivatives, and this fact is taken advantage of in the synthesis of many hydrocarbons. (See "Ethane," p. 24.)

# CHAPTER IV.

## OXYGEN DERIVATIVES OF METHANE AND ETHANE.

THERE are several classes of oxygen derivatives of the hydrocarbons. Among them are the important bodies known as alcohols, ethers, aldehydes, and acids. Each of these classes will be taken up in turn.

### 1. ALCOHOLS.

Among the most important oxygen derivatives are the alcohols, of which methyl alcohol, or wood spirits, and ethyl alcohol, or spirits of wine, are the best known examples. As far as composition is concerned, these bodies bear very simple relations to the two hydrocarbons, methane and ethane. These relations are indicated by the formulas, —

| Hydrocarbons. | Alcohols. |
|---|---|
| $CH_4$ | $CH_4O$ |
| $C_2H_6$ | $C_2H_6O$. |

The molecule of the alcohol differs from that of the corresponding hydrocarbon by one atom of oxygen. In order to understand the chemical nature of alcohols, it will be best to study with some care the reactions of one; and we may take for this purpose the simplest one of the series, viz., methyl alcohol.

**Methyl alcohol, $CH_4O$.** — This alcohol is known also as wood spirits. It is found in nature in combination in the oil of wintergreen. It is formed, together with many other substances, in the dry distillation of wood. It is hence contained in crude pyroligneous acid or wood vinegar. Wood is distilled in large quantities for various purposes; chiefly however, for making charcoal. In some charcoal factories the distillate is collected and utilized. Wood is distilled also for the purpose of making vinegar, or pure acetic acid.

It is not an easy matter to get pure methyl alcohol from crude wood spirits. Fractional distillation alone will not answer; though, if the mixture be distilled for some time, and the impure alcohol thus obtained then converted into some crystalline derivative, the latter can be purified and then decomposed in such a way as to yield the alcohol in pure condition.

Methyl alcohol is a liquid which boils at 66.7°, and has the specific gravity 0.8142 at 0°. It closely resembles ordinary alcohol in all its properties. It burns with a non-luminous flame. When taken into the system it intoxicates. In concentrated form it is poisonous. It is an excellent solvent for fats, oils, resins, etc., and is extensively used for this purpose.

1. *Action of hydrochloric, hydrobromic, and other acids on methyl alcohol.* The action of a few acids is represented by the following equations: —

$$\begin{aligned} CH_4O + HBr &= CH_3Br + H_2O; \\ CH_4O + HCl &= CH_3Cl + H_2O; \\ CH_4O + HNO_3 &= CH_3NO_3 + H_2O; \\ 2\ CH_4O + H_2SO_4 &= (CH_3)_2SO_4 + 2\ H_2O. \end{aligned}$$

The action is plainly suggestive of that of metallic hydroxides or bases. In each case the acid is neutralized and water is formed, just as the acid would be neutralized by potassium hydroxide.

2. *Action of phosphorus trichloride.* When phosphorus trichloride acts on methyl alcohol, the products are chlor-methane and phosphorous acid: —

$$3\ CH_4O + PCl_3 = 3\ CH_3Cl + P(OH)_3.$$

Here an atom of oxygen and an atom of hydrogen are together replaced by one atom of chlorine, the reaction being like that which takes place between water and phosphorus trichloride: —

$$3\ H_2O + PCl_3 = 3\ HCl + P(OH)_3.$$

This fact would lead us to suspect that there is some resemblance between the alcohol and water.

3. *Action of potassium and sodium.* When potassium is brought in contact with pure methyl alcohol, hydrogen is given off, and a compound containing potassium is formed: —

$$CH_4O + K = CH_3KO + H.$$

Further treatment of this compound with potassium causes no further evolution of hydrogen, so that plainly one of the four hydrogen atoms contained in methyl alcohol differs from the other three.

The resemblance between methyl alcohol and metallic hydroxides; the replacement of hydrogen and oxygen by chlorine; and the resemblance between the alcohol and water; and, finally, the replacement of one, and only one, hydrogen atom by potassium, lead to the conclusion that the alcohol contains hydrogen and oxygen in combination, and that the characteristic reactions are due to the presence of the group called ***hydroxyl*** (OH). The analogy between the alcohol, a metallic hydroxide, and water, is shown by these formulas: alcohol, $CH_3.OH$; hydroxide, $K.OH$; water $H.OH$. Thus water appears as the type of both the hydroxide and the alcohol, and they may be regarded as derived from water by replacing one hydrogen atom by the group $CH_3$, in the case of the alcohol, and the metal potassium in the case of the hydroxide. Or, on the other hand, methyl alcohol may be regarded as marsh gas in which one of the hydrogen atoms is replaced by hydroxyl. This is the view which is universally held.

To test the correctness of the view, we may try to make methyl alcohol in some way that will show us of what parts it is made up. Thus, we might start with marsh gas, and introduce a halogen, as bromine. Now, if we bring brom-methane together with a metallic hydroxide, the bromine and the metal may unite, leaving the hydroxyl and the group $CH_3$, which may unite also, as indicated in the equation

$$CH_3Br + MOH = CH_3.OH + MBr.$$

If methyl alcohol could be made in this way, we should have very clear proof of the correctness of the view expressed in the formula $CH_3.OH$. While no reaction of this kind has been used in the preparation of methyl alcohol, so many alcohols have been made in this way that the proof is overwhelming.

The reactions above considered show that the part of methyl alcohol which corresponds to the metal in the hydroxide is the group $CH_3$. This it is which enters into the acids in place of their hydrogen, and this remains unchanged when potassium acts upon the alcohol. It has received the name *methyl*. Hence we have the names methyl alcohol, methyl bromide, methyl ether, etc. A group which, like methyl, appears in a number of compounds is called a *radical*, or *residue*. These names are intended simply to designate that part of a carbon compound which remains unchanged when the compound is subjected to various transforming influences.

The two most characteristic reactions of methyl alcohol are: (1) its power to form salt-like, neutral bodies when treated with acids; and (2) its power to form an acid when oxidized.

The neutral bodies formed with acids correspond to the salts of metals, only they contain the radical, or residue, methyl, $CH_3$, in the place of metals. They are called *compound ethers* or *ethereal salts*.

The acid formed by oxidation has the composition expressed by the formula $CH_2O_2$. It differs from the alcohol by containing one atom of oxygen more and two atoms of hydrogen less. It will be shown that this acid is the first of an important series of acids, known as the *fatty acids*, each of which bears the same relation to a hydrocarbon containing the same number of carbon atoms that this simplest acid bears to marsh gas.

**Ethyl alcohol, $C_2H_5.OH$.** — This is the best known substance belonging to the class of alcohols. It is known also by the names *spirits of wine* and *ordinary alcohol*. It occurs in small quantities widely distributed in nature.

The one method of preparation upon which we are dependent for alcohol is the fermentation of sugar.

**Fermentation.** — Whenever a plant juice which contains sugar is left exposed to the air, it gradually undergoes a change by which it loses its sweet taste. Usually the change consists in a breaking up of the sugar into carbon dioxide and alcohol. The equation

$$\underset{\text{Sugar.}}{C_6H_{12}O_6} = 2\ \underset{\text{Alcohol.}}{C_2H_6O} + 2\ CO_2,$$

approximately expresses what takes place in the process which is known as *alcoholic fermentation.* It has been shown that fermentation is caused by the presence of small organized bodies, either animal or vegetable. These bodies, which are known as *ferments*, are of different kinds, and cause different kinds of fermentation with different products. Among the kinds of fermentation the following may be specially mentioned: —

1. *Alcoholic* or *vinous fermentation.* This is caused by a vegetable ferment which is contained in ordinary yeast. The ferment consists of small, round cells arranged in chains. The products of its action are alcohol and carbon dioxide.

2. *Lactic acid fermentation.* This is due to a vegetable ferment which is contained in sour milk. It has the power of transforming sugar into lactic acid.

3. *Acetic acid fermentation.* This is due to a peculiar vegetable ferment which acts upon alcohol, transforming it into acetic acid.

The germs of the various ferments are in the air; and, whenever they find favorable conditions, they develop and produce their characteristic effects. They will not develop in a solution of pure sugar. The variety of sugar which is fermentable, and which is the one from which alcohol is obtained, is not an ordinary cane sugar, but one known as *grape sugar*; or, more commonly, *glucose.* In order that the ferments may grow, there must be present in the solution, beside the sugar, substances which contain nitrogen. These, as well as the sugar, are contained in the juices pressed out from fruits, and hence these juices readily undergo fermentation.

In the manufacture of alcohol a solution containing either starch or sugar is first prepared from the residue of wine presses, or from some kind of grain or potatoes. In case the solution contains grape sugar, this undergoes fermentation directly when the ferment is added. If the substance in solution is cane sugar, this is first changed by the ferment into grape sugar, and the fermentation then takes place as in the first case.

**Experiment 7.** Dissolve 40 to 50$^g$ commercial grape sugar in 2 to 3 litres of water in a good-sized flask. Connect the flask by means of a bent tube with a cylinder containing clear lime water. Protect the latter from the air by means of a tube containing caustic potash. Now add to the solution of grape sugar a little brewer's yeast; close the connections, and allow to stand. Soon an evolution of gas will begin, and, as this passes through the lime water, a precipitate of calcium carbonate will be formed. After the action is over, place the flask in a water-bath; connect with a condenser, and distil over 100$^{cc}$ of the liquid. Examine this for alcohol.

A good way to detect alcohol is this: Warm the solution to be tested; add a small piece of iodine and then caustic potash until the color is destroyed. On cooling, a yellow crystalline powder of *iodoform* is deposited.

To obtain alcohol from fermented liquids, they must be distilled. The ordinary alcohol contains water, and a mixture of other alcohols called *fusel oil*. The latter can be removed partly by distillation, and the last portions can be gotten rid of by filtering through charcoal. The water cannot be removed completely by distillation, though a product containing about 93 per cent of alcohol may be obtained.

*Absolute alcohol* is ordinary alcohol from which the water has been removed to a considerable extent by means of quicklime. *As a rule absolute* alcohol contains about 5 per cent of water.

By continued treatment with lime the quantity of water may be reduced to one-half a per cent, and this small quantity may be removed by treatment with metallic sodium.

**Experiment 8.** Prepare absolute alcohol from ordinary strong alcohol. For this purpose a good-sized flask is one-half to two-thirds filled with quicklime broken into small lumps. The alcohol is poured upon the lime, and allowed to stand at least twenty-four hours, when it is distilled off on a water-bath. If the alcohol used contains considerable water, it is necessary to repeat the treatment with lime.

Pure ethyl alcohol has a peculiar, pleasant odor. It is claimed, however, that perfectly anhydrous alcohol has no odor. It remains liquid at very low temperatures, but has recently been converted into a solid at a temperature of −130.5°. It boils at 78.3°. It burns with a non-luminous flame, which does not leave a deposit of soot on substances placed in it. It may hence be used for heating purposes in chemical laboratories. When mixed with air its vapor explodes when a flame is applied. Its effects upon the human system are well known. It intoxicates when taken in dilute form, while in large doses it is poisonous. It lowers the temperature of the body from 0.5° to 2° when taken internally, although the sensation of warmth is experienced.

Alcohol is the principal solvent for substances of organic origin. It is hence extensively used in the arts, as in the manufacture of varnishes, perfumes, and tinctures of drugs.

The many beverages which are in use depend for their efficiency upon the presence of alcohol in greater or smaller quantity. The milder forms of beer contain from 2 to 3 per cent; light wines, such as claret, about 8 per cent; while whiskey, brandy, rum, and other distilled liquors sometimes contain as much as 60 to 75 per cent. These distilled liquors are nothing but ordinary alcohol with water and small quantities of substances obtained from the fruit or grain used in their preparation, or obtained by standing in barrels made of oak wood. The different flavors are due to the small quantities of these substances.

*Chemical conduct of ethyl alcohol.* All that was said in regard to the chemical conduct of methyl alcohol applies to ethyl alcohol. The action of acids, of phosphorus trichloride, of the alkali metals, and of oxidizing agents is the same as in the case of methyl alcohol, only the products formed contain the radical, ethyl, $C_2H_5$, instead of methyl.

NOTE FOR STUDENT. — The student is advised to write the equations representing the action of hydrochloric, hydrobromic, and nitric acids; of phosphorus trichloride; and of potassium, upon ethyl alcohol. What is the composition of the acid formed by oxidation of ordinary alcohol?

## 2. ETHERS.

As has been shown, when an alcohol is treated with potassium or sodium, compounds are formed having the formulas

$$CH_3ONa,\ CH_3OK,\ C_2H_5OK,\ C_2H_5ONa.$$

If one of these be treated with a mono-halogen derivative of a hydrocarbon, as, for example, iodo-methane, $CH_3I$, reaction takes place thus: —

$$CH_3ONa + CH_3I = C_2H_6O + NaI.$$

The reaction leaves very little room for doubt in regard to the structure of the compound $C_2H_6O$. It must be represented by the formula $CH_3 - O - CH_3$, or $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > O$, or $(CH_3)_2O$. Comparing it with methyl alcohol, we see that it is obtained from the alcohol by replacing the hydrogen of the hydroxyl by methyl, $CH_3$. Just as the alcohol is analogous to the hydroxide $KOH$, so the new compound is analogous to the oxide $K_2O$. It is the representative of a class of bodies known as *ethers*, which are analogous to the oxides of the metals. Our ordinary ether is the chief representative of the class.

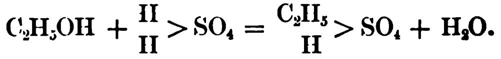
While the reaction above mentioned serves admirably to show the relations between the alcohols and ethers, it is not the one that is made use of in their preparation. This consists in treating the alcohols with sulphuric acid, and distilling.

**Ethyl ether, $C_4H_{10}O = (C_2H_5)_2O$.** — This is the substance commonly known simply as *ether*, or *sulphuric ether*. The latter name was originally given to it because sulphuric acid is used in its manufacture, and plainly not because any sulphur is contained in it.

Theoretically, the simplest way to make ether from alcohol is to make the sodium compound of alcohol, $C_2H_5ONa$, and to heat this with brom- or iodo-ethane thus: —

$$C_2H_5ONa + C_2H_5I = (C_2H_5)_2O + NaI.$$

Practically, however, ether may be made much more readily, and it is made on the large scale by mixing sulphuric acid and alcohol in certain proportions, and then distilling the mixture as described below. Two distinct reactions are involved in this process. First, when alcohol and sulphuric acid are brought together, half the hydrogen of the acid is replaced by ethyl thus: —

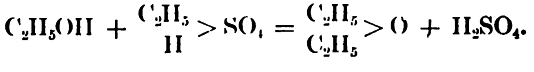


$$C_2H_5OH + \begin{matrix}H\\H\end{matrix}{>}SO_4 = \begin{matrix}C_2H_5\\H\end{matrix}{>}SO_4 + H_2O.$$

The product thus formed is called *ethyl-sulphuric acid*.

**Experiment 9.** Slowly pour 20 to 30cc concentrated sulphuric acid into about the same volume of alcohol of 80 to 90 per cent. Stir thoroughly, and dilute with a litre of water. In an evaporating dish add powdered barium carbonate until the liquid is neutral. Filter, and examine the clear filtrate for barium. Its presence shows that a soluble barium salt has been formed. This is barium ethyl-sulphate, $Ba(C_2H_5SO_4)_2$.

When ethyl-sulphuric acid is heated with alcohol, ether is formed, and sulphuric acid is regenerated thus: —



$$C_2H_5OH + \begin{matrix}C_2H_5\\H\end{matrix}{>}SO_4 = \begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O + H_2SO_4.$$

The ether thus formed distils over; and, if alcohol be admitted to the sulphuric acid, ethyl-sulphuric acid will again be formed, and with excess of alcohol it will yield ether. The actual method of procedure is described in

**Experiment 10.** Arrange an apparatus as shown in Fig. 6. In the flask put a mixture of 200g alcohol, and 360g ordinary concentrated sulphuric acid. It is better to mix them in another vessel, and allow the mixture to stand for some time until it is thoroughly cooled down; and then to pour off from the precipitated lead sulphate as completely as possible. Now heat until the thermometer indicates the temperature 140°. At this point the mixture boils, and ether begins to pass over. As soon as this is noticed, open the stop-cock of the vessel *A*, and let a slow stream of alcohol pass into the distilling flask through the tube *B*, which must reach beneath the surface of the mixture. Regulate this stream so that the temperature remains as near 140° as possible. In this way the operation can be kept up for a considerable time, the alcohol admitted to the flask passing out as ether, and being collected together with some alcohol in the receiver. After about a half litre to a litre of distillate has been collected, stop the operation. The mixture in the distilling flask may be kept in a stoppered bottle and used again when needed. Pour the distillate into a glass-stoppered

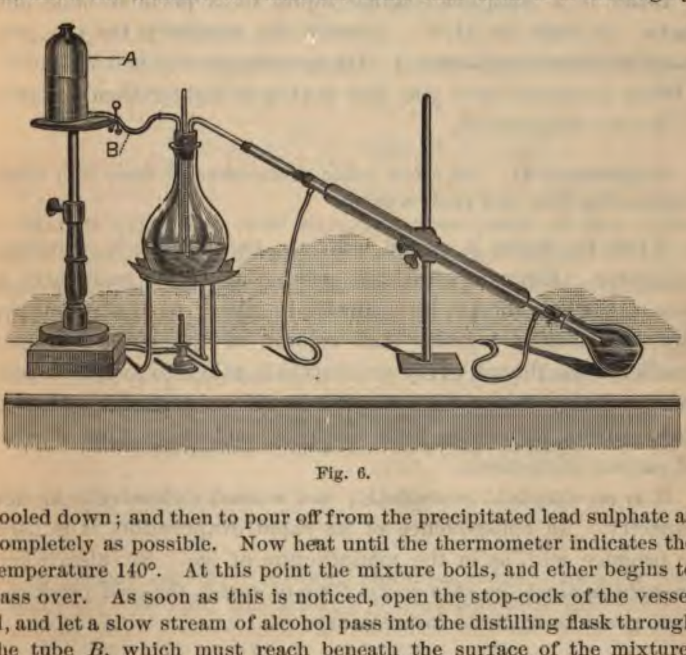


Fig. 6.

cylinder, and add water. The ether will rise to the top, forming a distinct layer, and may be removed by means of a pipette or separating funnel. It should be shaken in this way a few times with water; then treated with a little calcium chloride; and, after standing, poured off into a dry flask, and distilled on a water-bath.

N.B. *Never boil ether over a free flame; and, in working with it, always carefully avoid the neighborhood of flames. In boiling it on a water-bath, do not heat the water to boiling.*

Ether is a colorless, mobile liquid of a peculiar odor and taste. It boils at 34.9°. (Hence the necessity for the precautions mentioned above.) Its specific gravity is 0.736 at 0°. (What evidence have you had that it is lighter than water?) It is very inflammable.

**Experiment 11.** Put a few cubic centimetres of ether in a small evaporating dish, and apply a flame.

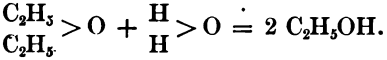
When its vapor is mixed with air, the mixture is extremely explosive. Ether is somewhat soluble in water, and water is also somewhat, though less, soluble in ether; so that when the two are shaken together the volume of the ether becomes smaller, even though every precaution is taken to avoid evaporation. Ether mixes with alcohol in all proportions. It is a good solvent for resins, fats, alkaloids, and many other classes of carbon compounds.

It is an excellent anæsthetic, and is used extensively in this capacity. In consequence of its rapid evaporation, it is used to produce cold, as in the manufacture of ice. So, also, when brought against the skin in the form of spray, the cold produced is so great as to cause insensibility.

**Experiment 12.** In a thin glass test-tube put $5^{cc}$ water. Introduce the tube into a small beaker containing some ether. Force air through the ether by means of a bellows. The water will be frozen.

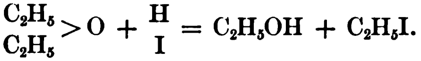
*Chemical conduct of ether.* If we were dependent upon the decompositions and general reactions of ether for our knowledge of its structure, we would be left in grave doubt as to the relations existing between it and alcohol. Its decompositions are mostly deep-seated, and not easily explained. Fortunately, as we have seen, its synthesis from sodium ethylate, $C_2H_5ONa$, and iodo-ethane, $C_2H_5I$, leaves us in no doubt regarding its structure. The simplest decompositions are these: —

Heated with water and a small quantity of sulphuric acid to 150°, it is converted into alcohol: —



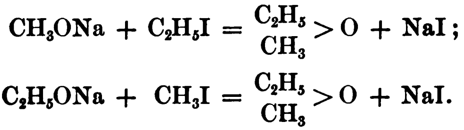
$$\begin{array}{c}C_2H_5\\C_2H_5\end{array}>O + \begin{array}{c}H\\H\end{array}>O = 2\ C_2H_5OH.$$

Treated with hydriodic acid at a low temperature, alcohol and iodo-ethane are formed: —



$$\begin{array}{c}C_2H_5\\C_2H_5\end{array}>O + \begin{array}{c}H\\I\end{array} = C_2H_5OH + C_2H_5I.$$

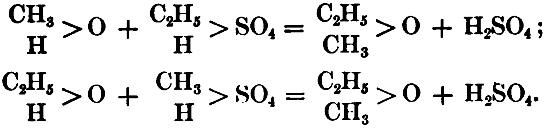
**Mixed ethers.** — Just as ordinary or ethyl alcohol yields ethyl ether, so methyl alcohol yields methyl ether, $(CH_3)_2O$. By modifying the method, a *mixed ether*, *methyl-ethyl ether*, $\begin{array}{c}C_2H_5\\CH_3\end{array}>O$, may be obtained. This is formed by treating sodium methylate with iodo-ethane, or by treating sodium ethylate with iodo-methane: —



$$CH_3ONa + C_2H_5I = \begin{array}{c}C_2H_5\\CH_3\end{array}>O + NaI;$$

$$C_2H_5ONa + CH_3I = \begin{array}{c}C_2H_5\\CH_3\end{array}>O + NaI.$$

It is formed also by distilling methyl alcohol with ethyl-sulphuric acid, or ethyl alcohol with methyl-sulphuric acid: —



$$\begin{array}{c}CH_3\\H\end{array}>O + \begin{array}{c}C_2H_5\\H\end{array}>SO_4 = \begin{array}{c}C_2H_5\\CH_3\end{array}>O + H_2SO_4;$$

$$\begin{array}{c}C_2H_5\\H\end{array}>O + \begin{array}{c}CH_3\\H\end{array}>SO_4 = \begin{array}{c}C_2H_5\\CH_3\end{array}>O + H_2SO_4.$$

Methyl ether and methyl-ethyl ether are very similar to ordinary ether.

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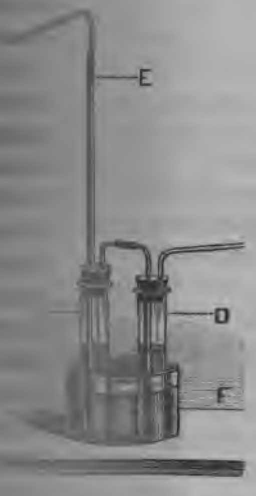

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## 3. ALDEHYDES.

It has been stated above that when methyl and ethyl alcohols are oxidized, they are converted into acids having the formulas $CH_2O_2$ and $C_2H_4O_2$, respectively. By proper precautions, products can be obtained intermediate between the alcohols and acids, and differing from them in composition in that they contain two atoms of hydrogen less than the corresponding alcohols. These products are called *aldehydes*, from *alcohol dehydrogenatum*, from the fact that they must be regarded as alcohols from which hydrogen has been abstracted. The relations in composition between the hydrocarbons, alcohols, and aldehydes are shown by these formulas:—

| Hydrocarbons. | Alcohols. | Aldehydes. |
|---|---|---|
| $CH_4$ | $CH_4O$ | $CH_2O$ |
| $C_2H_6$ | $C_2H_6O$ | $C_2H_4O$ |
| etc. | etc. | etc. |

**Methyl aldehyde, formic aldehyde, $CH_2O$.**—This is made by gentle oxidation of methyl alcohol, as by passing the vapor of the alcohol with air over a heated platinum spiral. It is a very volatile liquid, which, up to the present, has not been prepared in pure condition.

In order to gain a clear insight into the nature of the aldehydes, it will be best to study the best-known representative of the class, which is ethyl aldehyde.

**Ethyl aldehyde, acetic aldehyde, $C_2H_4O$.**—The name *ethyl aldehyde* is intended to recall the connection between the substance and ethyl alcohol; while the name *acetic aldehyde* is given to it because, by further oxidation, it is converted into acetic acid. The latter is perhaps the better name, as the aldehyde really does not contain ethyl, $C_2H_5$, as is evident from its molecular formula.

*Acetic aldehyde* is formed whenever alcohol is brought in contact with an oxidizing mixture; as, for example, potassium bichromate and dilute sulphuric acid.

**Experiment 13.** Dissolve a little potassium bichromate in water, and add sulphuric acid. Now add a few cubic centimetres of alcohol, and notice the odor, which is that of aldehyde. Notice, also, the change of color of the solution, showing the reduction of the chromate.

As aldehyde is a very volatile liquid, it is difficult to collect it. In preparing it, it is therefore better to pass it into some liquid which will absorb it, and then afterwards separate it by some appropriate method. A good method is that described below.

**Experiment 14.** Arrange an apparatus as shown in Fig. 7. Put 120g granulated potassium bichromate in the flask *A*, which must have a capacity of 1½ to 2 litres. Make a mixture of 160g concentrated sulphuric acid, 480g water, and 120g alcohol. Cool the mixture down to the ordinary temperature, and then pour it *slowly* through the funnel-tube *B* into the flask containing the potassium bichromate. The

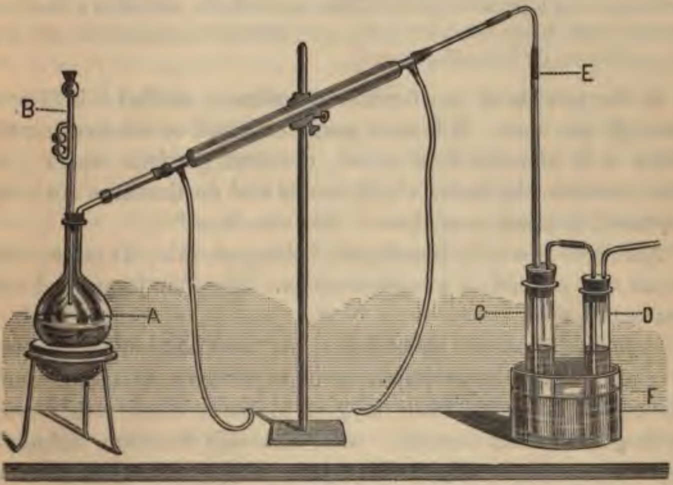


Fig. 7.

flask should stand on a water-bath containing cold water. The cylinders *C* and *D* are about half filled with ordinary ether, each one containing about $200^{cc}$ ether, and placed in the large vessel *F*, which contains ice water.

Usually, when the alcohol, water, and sulphuric acid are poured upon the bichromate, the action begins without application of heat. At times it takes place rapidly, so that the liquid should always be added slowly. The aldehyde which is thus formed, together with some alcohol and water vapor, passes into the condenser-tube, where the greater part of the alcohol and water is condensed and returned to the flask, while the aldehyde, being much more volatile, passes into the ether and is there absorbed. After the action is over, the distilling vessel and condenser are removed, and, at *E*, connection is made with an apparatus furnishing *dry* ammonia gas. The gas is passed into the cold ethereal solution of aldehyde to the point of saturation. A beautifully crystallized compound of aldehyde and ammonia, known as *aldehyde-ammonia*, is deposited. The ether is poured off, and the crystals placed on filter-paper. They gradually undergo change in the air, becoming yellow, and acquiring a peculiar odor. If the crystals are placed in a flask and treated with dilute sulphuric acid, pure aldehyde passes over, and may be condensed by ice-cold water.

In the process of purification of ordinary alcohol it is filtered through charcoal. It is thus partly oxidized to aldehyde; and, when it is afterwards distilled, the first portions which pass over contain aldehyde, which is obtained on the large scale by repeated distillation of these "first runnings."

Aldehyde is a colorless liquid, boiling at 21°. It mixes with water and alcohol in all proportions. Its odor is marked and characteristic.

From the chemical stand-point, the most characteristic property of aldehyde is its power to unite directly with other substances. It unites with oxygen to form acetic acid; with hydrogen to form alcohol; with ammonia to form *aldehyde-ammonia*, $C_2H_4O.NH_3$; with hydrocyanic acid to form *aldehyde hydrocyanide*, $C_2H_4O.HCN$; with the acid sulphites of the alkalies forming compounds represented by the formulas $C_2H_4O.HKSO_3$ and $C_2H_4O.HNaSO_3$; and with other substances. Indeed, if left to itself, it readily changes into polymeric modifications, uniting with itself to form more complex bodies, *paraldehyde* and *metaldehyde*.

**Paraldehyde, $C_6H_{12}O_3$.** — This is formed by adding a few drops of concentrated sulphuric acid to aldehyde, which causes the liquid to become hot. On cooling to 0°, the paraldehyde solidifies in crystalline form. It melts at 10.5°. It dissolves in eight times its own volume of water. Boils at 124°. When distilled with dilute sulphuric acid, hydrochloric acid, etc., it is converted into aldehyde. The specific gravity of its vapor has been found to be 4.583. This leads to the molecular weight 132.4, and consequently to the formula $C_6H_{12}O_3$. It is called a polymeric modification of aldehyde. The cause of the peculiar action, and the structure of the product are not known.

**Metaldehyde, $(C_2H_4O)_x$.** — Metaldehyde is formed in much the same way as paraldehyde, only a low temperature (below 0°) is most favorable for its formation. It crystallizes in needles, which are insoluble in water, and but slightly soluble in alcohol, chloroform, and ether in the cold, though more readily at a slightly elevated temperature. When heated to 120° in a sealed tube, it is converted into aldehyde. Hence its vapor density cannot be determined, and its molecular weight is unknown. It has the same composition as aldehyde and paraldehyde, but it is probably more complex than the latter; that is, its molecule is probably made up of a larger number than three molecules of aldehyde. Distilled with dilute sulphuric acid, etc., it is easily converted into aldehyde.

In consequence of the tendency of aldehyde to unite with oxygen, it is a strong reducing agent. When added to an ammoniacal solution of silver nitrate, metallic silver is deposited on the walls of the vessel in the form of a brilliant mirror.

**Experiment 15.** To a weak aqueous solution of aldehyde, or of aldehyde-ammonia, in a test-tube, add a few drops of ammonia and of a solution of silver nitrate. Warm gently; and, when the deposit on the walls of the tube begins to appear, stop heating. A brilliant mirror of metallic silver will appear. This method is used in the manufacture of mirrors. What becomes of the aldehyde?

*Chemical transformations of aldehyde.* As aldehyde is produced from alcohol by oxidation, so alcohol can be formed from aldehyde by reduction: —

$$C_2H_6O + O = C_2H_4O + H_2O;$$
$$C_2H_4O + H_2 = C_2H_6O.$$

By oxidation aldehyde is converted into an acid of the formula $C_2H_4O_2$, which is acetic acid; and, by reduction, acetic acid is converted into aldehyde: —

$$C_2H_4O + O = C_2H_4O_2;$$
$$C_2H_4O_2 + H_2 = C_2H_4O + H_2O.$$

Treated with phosphorus pentachloride, aldehyde yields *ethylidene chloride*, $C_2H_4Cl_2$ (which see). This reaction is of special interest and importance, as it helps us to understand the relation between aldehyde and alcohol. Alcohol, as has been shown, is the hydroxide of ethyl, $C_2H_5.OH$. When oxidized it loses two atoms of hydrogen. Is the hydrogen of the hydroxyl one of the two which are given off? If so, what readjustment of the oxygen takes place? Such are the questions which we have a right to ask.

To understand the action of phosphorus pentachloride on aldehyde, it will be necessary to consider briefly the action of this reagent in general upon compounds containing oxygen. When it is brought in contact with water, the first change is represented by the equation

$$H_2O + PCl_5 = POCl_3 + 2\ HCl.$$

Next, the oxichloride, $POCl_3$, is acted upon thus: —

$$3\ H_2O + POCl_3 = PO(OH)_3 + 3\ HCl.$$

Or, expressing both changes in one equation, we have: —

$$4\ H_2O + PCl_5 = PO(OH)_3 + 5\ HCl.$$

The phosphorus pentachloride gives up its chlorine and takes up oxygen, or oxygen and hydrogen, in its place. This is the general tendency of the chlorides of phosphorus.

Now, when a chloride of phosphorus is brought together with an alcohol, the oxygen is replaced by chlorine, two atoms of the latter for one of the former, thus: —

$$C_2H_5.OH + PCl_5 = C_2H_5Cl.ClH + POCl_3.$$

But as hydroxyl, $-O-H$, is univalent, its place cannot be taken by two atoms of chlorine and one of hydrogen, and the two chlorine atoms have not the power of linking the hydrogen to the ethyl. Hydrochloric acid is given off, and a compound is formed, which may be regarded as alcohol in which one chlorine atom takes the place of the hydroxyl. This is the kind of action which takes place whenever a chloride of phosphorus acts upon a compound containing hydroxyl; and *we hence make use of the reaction for determining whether hydroxyl is or is not present in a compound.*

When aldehyde is treated with phosphorus pentachloride, the action is entirely different from that just described. Instead of a hydrogen and an oxygen atom being replaced by one chlorine, *the oxygen atom alone is replaced by two chlorine atoms:* —

$$C_2H_4O + PCl_5 = C_2H_4Cl_2 + POCl_3.$$

If the explanation above offered of the action of phosphorus pentachloride on alcohol is correct, it follows that aldehyde is not a hydroxyl compound. We can readily understand why the oxygen atom should be replaced by two chlorine atoms, if it is in combination only with carbon as in carbon monoxide, $CO$. There is an essential difference between this kind of combination and that which we have in hydroxyl as $C-O-H$. In the latter condition the oxygen serves to connect carbon with hydrogen; in the former it is in combination only with the carbon, and, presumably, the force which holds it can also hold two atoms of chlorine or of any other univalent element with which it can unite. So that, if oxygen be in a compound in the carbon monoxide condition, we would expect it to be replaced by two atoms of chlorine when the compound is treated with phosphorus pentachloride. Let R.CO represent any such compound; then we would have: —

$$RCO + PCl_5 = R.CCl_2 + POCl_3;$$

while, when oxygen is present in the hydroxyl condition, we have: —

$$R.C - O - H + PCl_5 = R.CCl + POCl_3 + HCl.$$

Just as the latter reaction is used to detect the presence of hydroxyl oxygen, so the former is used to detect oxygen in the other condition, which is commonly known as the ***carbonyl*** condition.

In terms of the valence hypothesis, it is said that in the hydroxyl compounds oxygen is in combination with carbon with one of its affinities, and with hydrogen with the other, while in the carbonyl compounds it is in combination with carbon with both its affinities as represented thus, $C = O$.

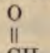
According to the above reasoning aldehyde is a carbonyl compound, or it contains the group CO. The simplest aldehyde must therefore be represented by the formula $H_2C = O$. Its homologue, acetic aldehyde, is $CH_3.\overset{\overset{O}{\|}}{C} - H$. The peculiar properties of aldehyde are believed to be due to the presence of this group, $\overset{\overset{O}{\|}}{C} - H$, which is called the aldehyde group. We do not know that the double line in the formula conveys any correct idea in regard to the relation between the carbon and oxygen. All that we know is that these two elements do occur in two different relations to each other, and the formulas $C - O - H$ and $C = O$ recall these relations. They are expressions of facts established by experiment. Our notions in regard to these relations are largely dependent upon the reactions with the *chlorides of phosphorus* referred to above.

**Chloral, trichloraldehyde, $CCl_3.CHO$.** — When chlorine acts directly upon aldehyde, complicated reactions take place which need not be considered here. If, however, water and calcium carbonate are present, substitution takes place, and *trichloraldehyde* is formed. When alcohol is treated with chlorine, a double action takes place: 1st. The alcohol is changed to aldehyde thus: —

$$CH_3.CH_2OH + Cl_2 = CH_3.COH + 2\ HCl.$$

Then the chlorine acts upon the aldehyde, replacing the three hydrogens of the methyl, forming trichloraldehyde: —

$$CH_3.COH + 6\ Cl = CCl_3.COH + 3\ HCl.$$

In reality the aldehyde first formed acts upon the alcohol, forming an intermediate product which is acted upon by the chlorine. The chlorine product thus formed breaks up, forming chloral. The essential features of the reaction, however, are stated in the above equations. Trichloraldehyde is the substance commonly known as chloral. It is simply the tri-chlorine substitution product of aldehyde. It has all the general properties of aldehyde, and the conclusion is therefore justified that it contains the aldehyde group  $-\overset{\overset{O}{\|}}{C}H$.

Chloral is a colorless liquid, which boils at 94°, and has the specific gravity 1.5.

NOTE FOR STUDENT. — Give the formulas of compounds formed when chloral is brought together with ammonia, hydrocyanic acid, and the acid sulphites of the alkalies. What is the formula of the acid formed by its oxidation? The answer is given in the statement that the general chemical conduct of chloral is the same as that of aldehyde.

When chloral and water are brought together, they unite to form a crystallized compound, *chloral hydrate*, $C_2HCl_3O + H_2O$, which is easily soluble in water, and crystallizes from the solution in beautiful, colorless, monoclinic prisms. It melts at 46°.

Taken internally in doses of from 1.5 to 3g. it produces sleep. In larger doses it acts as an anaesthetic.

When treated with an alkali, chloral and chloral hydrate break up, yielding chloroform and formic acid: —

$$\underset{\text{Chloral.}}{CCl_3.COH} + KOH = \underset{\text{Chloroform.}}{CHCl_3} + \underset{\text{Potassium formate.}}{KCHO_2}.$$

This reaction, taken together with those which give chloral from alcohol, enables us to understand the reaction which is used in making chloroform and iodoform.

NOTE FOR STUDENT. — How is chloroform made? How may the method be explained? Answer the same questions for iodoform. The bleaching powder used in preparing chloroform furnishes chlorine. Is an alkali present?

### 4. ACIDS.

When methyl and ethyl alcohols are oxidized, they are converted first into aldehydes, and then the aldehydes take up oxygen and are converted into acids. The relations in composition between the hydrocarbons, alcohols, aldehydes, and acids are shown in the subjoined table: —

| Hydrocarbons. | Alcohols. | Aldehydes. | Acids. |
|---|---|---|---|
| $CH_4$ | $CH_4O$ | $CH_2O$ | $CH_2O_2$ |
| $C_2H_6$ | $C_2H_6O$ | $C_2H_4O$ | $C_2H_4O_2$ |
| etc. | etc. | etc. | etc. |

The two acids whose formulas are here given are the well-known substances, *formic* and *acetic acids*.

**Formic acid, $CH_2O_2$.** — This acid occurs in nature in red ants, in stinging nettles, in the shoots of some of the varieties of pine, and elsewhere.

It may be prepared by distilling red ants, but is best prepared by heating oxalic acid with glycerin. Oxalic acid has the composition represented by the formula $C_2H_2O_4$. When heated in glycerin, the effect is to break it up into carbon dioxide and formic acid: —

$$C_2H_2O_4 = CO_2 + CH_2O_2.$$

The formic acid distils over, and may be condensed.

**Experiment 16.** Into a flask of 500 to 600$^{cc}$ capacity put 200 to 300$^{cc}$ anhydrous glycerin, and then add 30 to 40$^{g}$ crystallized oxalic acid. Connect the flask with a condenser, and insert a thermometer through the cork so that the bulb is below the surface of the glycerin. Heat gently. When the temperature reaches 75° to 90°, carbon dioxide will be given off. Dilute formic acid then distils over. When the evolution of carbon dioxide stops, add another portion of crystallized oxalic acid, and heat again. This operation may be repeated a number of times without renewing the glycerin; but, when about 100$^{g}$ of oxalic acid have been decomposed, enough formic acid for the purpose will have been formed. Dilute the distillate to about half a litre, and, while gently warming it in an evaporating dish, add freshly precipitated and washed copper oxide in small quantities until no more is dissolved. Then filter, and evaporate the solution to crystallization. The beautifully crystallized salt thus obtained is copper formate.

The formation of formic acid by oxidation of methyl alcohol, and by treatment of chloral with an alkali, has already been mentioned. The following methods are of special interest: —

(1) By the action of carbon monoxide upon potassium hydroxide: —

$$CO + KOH = H.CO_2K.$$

This method may be used for the preparation of formic acid on the large scale. Soda-lime acts as well as potassium hydroxide.

(2) By the action of metallic potassium upon moist carbon dioxide (carbonic acid): —

$$2\,CO_2 + K_2 + H_2O = HCO_2K + HCO_3K,$$

or $$2\,CO_3H_2 + K_2 = HCO_2K + HCO_3K + H_2O.$$

(3) By treatment of a solution of ammonium carbonate with sodium amalgam: —

$$CO_3(NH_4)_2 + 2\,H = HCO_2(NH_4) + H_2O + NH_3,$$

and $HCO_2(NH_4) + NaOH = HCO_2Na + NH_3 + H_2O.$

According to these last two methods formic acid appears as a reduction product of carbonic acid formed by the abstraction of one atom of oxygen: —

$$H_2CO_3 = H_2CO_2 + O.$$

It is extremely important to bear this fact in mind, as it is of great assistance in enabling us to understand the relation existing between the two acids, and between them and all other acids of carbon. It will be shown that all the acids of carbon may be regarded as derivatives of either formic acid or carbonic acid.

(4) When hydrocyanic acid is left in the presence of an acid or an alkali, it breaks up, forming ammonia and formic acid. The reaction may be represented thus: —

$$HCN + 2\,H_2O = H_2CO_2 + NH_3.$$

Of course, if an acid is present, the ammonium salt of the acid is formed; and, if an alkali is present, the formate of this alkali is formed. *A reaction similar to this is used very extensively in the preparation of the acids of carbon*, as will be shown.

Anhydrous formic acid may be made by dehydrating either the copper or lead salt, and passing dry hydrogen sulphide over the salt placed in a heated tube. The acid distils over, and may be obtained perfectly pure by placing a little of the anhydrous salt in it and redistilling.

It is a colorless liquid which boils at 99.9°. It has a penetrating odor. Dropped on the skin, it causes extreme pain and produces blisters. Its specific gravity at 0° is 1.22. When cooled down it solidifies to a mass of crystals which melt at 8.6°.

Concentrated sulphuric acid decomposes it into carbon monoxide and water: —

$$H_2CO_2 = CO + H_2O.$$

It is easily oxidized to carbonic acid. Hence it acts as a reducing agent. Heated with the oxides of mercury or silver, they are reduced to the metallic condition: —

$$HgO + H_2CO_2 = Hg + H_2O + CO_2.$$

Like other acids, formic acid yields a large number of salts with bases, and ethereal salts or compound ethers with the alcohols. These derivatives need not be considered here. The salts are all soluble in water, and some of them, as the lead, copper, and barium salts, crystallize very well. Some of the compound ethers will be mentioned when these substances are considered as a class.

**Acetic acid, $C_2H_4O_2$.** — The two methods by which acetic acid is exclusively made are, —

(1) By the oxidation of alcohol; and
(2) By the distillation of wood.

When pure alcohol is exposed to the air it undergoes no change. If, however, some platinum black be placed in it, oxidation takes place and acetic acid is formed. So also if fermented liquors which contain nitrogenous substances be exposed to the air, oxidation takes place, and the liquor becomes sour in consequence of the formation of acetic acid. A great deal of acetic acid is made by exposing poor wine to the action of the air. The product is known as *wine vinegar*. The formation of vinegar has been shown to be due to the presence of a microscopic organism (*Mycoderma aceti*) commonly known as "mother-of-vinegar." This serves in some way to convey the oxygen from the air to the alcohol. The "quick-vinegar process," much used in the manufacture of vinegar, consists in allowing weak spirits of wine to pass slowly through barrels filled with beech shavings which have become covered with *Mycoderma aceti.* The presence of the organism is secured by first pouring strong vinegar into the barrels, and allowing it to stand for one or two days in contact with the shavings.

When wood is distilled, a very complex mixture passes over, one of the constituents being acetic acid. By keeping the temperature down comparatively low, the amount of acetic acid obtained is increased. The distillate is neutralized with soda ash, and the solution of crude sodium acetate thus obtained evaporated to dryness. It is then treated with sulphuric acid, and distilled, when acetic acid passes over.

Besides the two methods mentioned, there are two others which may be used for making acetic acid. One of them is a modification of a method referred to under formic acid, and, from the scientific stand-point, both are of great interest. They are, —

(1) By treating carbon dioxide with a compound known as *sodium-methyl*, which may be regarded as marsh gas, in which one hydrogen is replaced by sodium as shown in the formula $CH_3Na$.

$$CO_2 + CH_3Na = CH_3.CO_2Na.$$

(2) By treating methyl cyanide, $CH_3CN$, with an acid or an alkali: —

$$CH_3CN + 2\,H_2O = CH_3.CO_2H + NH_3.$$

This reaction is analogous to that involved in the formation of formic acid from hydrocyanic acid (see p. 56).

Whether the acid is made from alcohol or from wood, it must be purified. For this purpose it is passed through charcoal and distilled. It still contains water, from which it cannot be completely separated by distillation. When cooled down to a sufficiently low temperature it solidifies, and the water may then partly be poured off. By repeating the freezing, and distilling a few times, perfectly pure, anhydrous acetic acid may be obtained.

**Experiment 17.** Make pure acetic acid from the commercial substance. First distil in fractions until a portion is obtained that boils between 110° and 119°. Put the vessel containing this in ice. The liquid will solidify almost completely. Pour off the little liquid which remains, and distil.

Acetic acid is a clear, colorless liquid, which boils at 119°. It has a very penetrating, pleasant, acid odor, and a sharp acid taste. *The pure substance acts upon the skin like formic acid, causing pain and raising blisters.* It solidifies when cooled down, and the crystals melt at 16.7°. The pure acid which is solid at temperatures below 16° is known as *glacial acetic acid.* Its specific gravity is 1.08 at 0°. It mixes with water in all proportions.

Acetic acid is extensively used, chiefly in the dilute, impure form known as vinegar. Formic acid would answer perhaps as well. It is used in calico printing in the form of iron and aluminium salts. With iron it gives hydrogen, which is needed in the manufacture of certain compounds used in making dyes, as, for example, aniline. It is an excellent solvent for many organic substances, and is therefore frequently used in scientific researches.

*Derivatives of acetic acid.* Acetic acid yields a very large number of derivatives. They may be considered briefly under two heads: (1) Those which are formed in consequence of the acid properties and which necessitate a loss of the acid properties, as the salts, ethereal salts, etc.; and (2) those in which the acid properties remain unchanged.

*Salts of acetic acid.* The acetates of the alkalies were the first compounds of carbon ever prepared. The *potassium* and *sodium* salts are used in the chemical laboratory. Both crystallize, the sodium salt particularly well and easily.

*Lead acetate*, $(C_2H_3O_2)_2Pb$. This salt, which is commonly known as *sugar of lead*, is made on the large scale by dissolving lead oxide in acetic acid. It crystallizes well, and is soluble in 1.5 parts of water at ordinary temperatures. Commercial *sugar of lead* frequently contains an excess of lead oxide in the form of basic salts. A solution of such a mixture becomes turbid when allowed to stand in the air, or gives a precipitate when dissolved in ordinary spring water, in consequence of the formation of lead carbonate.

*Copper acetate*, $(C_2H_3O_2)_2Cu$. This salt may be made by dissolving copper hydroxide or carbonate in acetic acid. It crystallizes in dark-blue, transparent prisms. A *basic acetate*, formed by the action of acetic acid on copper in the air, is known as *verdigris*.

*Copper aceto-arsenite*, $3\,CuAs_2O_4 + (C_2H_3O_2)_2Cu$. This double salt is formed by boiling verdigris and arsenic trioxide together in water. It has a fine bright-green color, and is used as a coloring matter. It is the chief constituent of emerald green, or Schweinfurt's green.

Iron forms two distinct salts with acetic acid, the *ferrous* salt, $(C_2H_3O_2)_2Fe + 4\,H_2O$, and the *ferric* salt, $(C_2H_3O_2)_6Fe_2$. The latter is formed when sodium acetate is added to an acidified solution of a ferric salt. At first the solution becomes deep-red in color; but, on boiling, all the iron is precipitated as a basic salt. Hence this salt is used for the purpose of separating iron from manganese in analytical operations.

**Experiment 18.** To a dilute solution of ferric chloride, contained in a small flask, add a little sulphuric acid and a solution of sodium acetate. Boil the red solution, and the basic iron salt is precipitated, leaving the solution colorless. Filter, and examine the filtrate for iron.

The ethereal salts will be mentioned briefly when this class of bodies is considered. The principal one is *ethyl acetate* or *acetic ether*, which is formed from acetic acid and ordinary alcohol. When a mixture of these two substances is treated with sulphuric acid, the ether is formed and may be recognized by its pleasant odor. This fact is taken advantage of for the detection of acetic acid.

**Experiment 19.** To a mixture of about equal parts of acetic acid and alcohol, in a test-tube, add a little concentrated sulphuric acid, and *notice the odor. It is* that of ethyl acetate or acetic ether.

**Acetic anhydride or acetyl oxide, $C_4H_6O_3$.** — This substance, which bears to acetic acid the relation of an anhydride, is made by abstracting water from the acid.

$$2\,C_2H_4O_2 = C_4H_6O_3 + H_2O.$$

Like other acids, acetic acid contains hydroxyl, as will be shown below. We may hence represent the acid thus: $C_2H_3O.OH$. The part $C_2H_3O$ is known as acetyl. Now when water is abstracted from the acid, the change takes place as represented in this equation: —

$$\left.\begin{matrix} C_2H_3O.OH \\ C_2H_3O.OH \end{matrix}\right\} = \left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O + H_2O.$$

Hence, according to this, acetic anhydride appears as the oxide of acetyl, while the acid itself is the hydroxide.

Acetic anhydride is a colorless liquid which boils at 138°. With water it gives acetic acid.

**Acetyl chloride, $C_2H_3OCl$.**
**Acetyl bromide, $C_2H_3OBr$.**
**Acetyl iodide, $C_2H_3OI$.**

Just as alcohol, when treated with phosphorus trichloride, yields a chloride of ethyl, so acetic acid, when treated with the same reagent, yields acetyl chloride. The character of the reaction is the same in both cases. It consists in the replacement of hydroxyl by chlorine.

$$3\,C_2H_3O.OH + PCl_3 = \underset{\text{Acetyl chloride.}}{3\,C_2H_3OCl} + P(OH)_3.$$

**Experiment 20.** Arrange a *dry* distilling flask, with condenser and *dry* receiver, under a hood or out of doors. Bring together 9 parts (say $180^g$) strong acetic acid and 6 parts (say $120^g$) phosphorus trichloride. Slightly heat the mixture on the water-bath, when acetyl chloride will distil over. Collect in a dry bottle.

Acetyl chloride is a colorless liquid which boils at 55°. Water acts upon it very readily, acetic and hydrochloric acids being formed: —

$$C_2H_3OCl + H_2O = C_2H_3O.OH + HCl.$$

In this case the chlorine is replaced by hydroxyl. As the substance is volatile, it fumes in contact with the air in consequence of the formation of hydrochloric acid. It must be kept in tightly-stoppered bottles. In handling it, care must be taken not to bring it near the nose, as its odor is very suffocating, and it attacks the mucous membranes of the eyes and nose, producing coughing and other bad results.

Acetyl chloride is a valuable reagent much used in the examination of compounds of carbon. Its value depends upon its action towards alcohols. When it is brought together with an alcohol, as, for example, methyl alcohol, hydrochloric acid is evolved, and the acetyl group takes the place of the hydrogen of the alcoholic hydroxyl: —

$$CH_3.OH + C_2H_3OCl = CH_3.O.C_2H_3O + HCl.$$

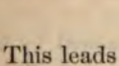
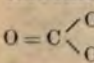
The product is an ethereal salt, methyl acetate. This kind of action takes place whenever an alcohol is treated with acetyl chloride. Hence if, on treating a body with acetyl chloride, its composition is changed, showing that hydrogen is replaced by acetyl, we are justified in concluding that the body contains alcoholic hydroxyl. The bromide and iodide resemble the chloride very closely.

**Experiment 21.** Treat a few cubic centimetres of *absolute* alcohol with acetyl chloride. Notice the evolution of hydrochloric acid and the odor of ethyl acetate.

*Substitution-products of acetic acid.* These bear the same relation to acetic acid that the substitution-products of marsh gas bear to marsh gas. They are formed by the simple substitution of a halogen, etc., for hydrogen. Only three of the four hydrogen atoms of acetic acid are capable of direct replacement. The fourth is the one to which the acid properties are due. Hence the substitution-products are acid. The best known of these products are the chlor-acetic acids which are made by treating the acid with chlorine. They are *mono-chlor-acetic*, *di-chlor-acetic*, and *tri-chlor-acetic acids.* Their formation is represented by the following equations: —

$$C_2H_3O.OH + Cl_2 = C_2H_2ClO.OH + HCl;$$
$$C_2H_2ClO.OH + Cl_2 = C_2HCl_2O.OH + HCl;$$
$$C_2HCl_2O.OH + Cl_2 = C_2Cl_3O.OH + HCl.$$

When treated with nascent hydrogen they are converted back into acetic acid. They yield salts, ethereal salts, anhydrides, etc., just the same as acetic acid itself.

*Theory in regard to the relations between the acids, alcohols, aldehydes, and hydrocarbons.* The reactions and methods of formation of acetic acid enable us to form a clear conception in regard to the relation of its constituents. In the first place the presence of hydroxyl is shown by the reaction with phosphorus trichloride. We hence have $C_2H_3O.OH$ as the formula representing this idea. But several questions still remain to be answered. There is another oxygen atom to be accounted for; and the relations between the hydroxyl and this oxygen must be determined if possible. The fact that this second oxygen is not readily replaced by chlorine indicates that it is not present as hydroxyl, and all methods of testing for hydroxyl fail to show its presence in acetyl chloride. Hence we may conclude that the second oxygen atom is present as carbonyl CO. This leads us to the formula  $H-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$ for the simplest acid, or formic acid. Accordingly, formic acid appears as carbonic acid, which we commonly represent by the formula  $O=C\langle{}^{OH}_{OH}$, in which one hydroxyl has been reduced to hydrogen. We have already seen that this reduction can be accomplished without difficulty. Many other arguments might be brought forward in favor of the view that the above formulas express the relations between formic and carbonic acids. Now, as *acetic acid is the* homologue of formic acid, we have every reason to believe that it differs from the latter in that it contains methyl in place of the hydrogen, which is in direct combination with carbon. It must hence be represented by the formula $CH_3.\overset{\overset{O}{\|}}{C}-OH$ or $CO\begin{matrix}\diagup CH_3 \\ \diagdown OH\end{matrix}$. The common constituent of the two acids, is the group $\overset{\overset{O}{\|}}{C}-O-H$ or $-CO.OH$, which is generally known as *carboxyl.* Acetic acid is closely related not only to formic but to carbonic acid. It may be regarded as carbonic acid, $CO\begin{matrix}\diagup OH \\ \diagdown OH\end{matrix}$, in which one hydroxyl is replaced by the radical methyl. In a similar way we shall see that all organic acids may be regarded as derived either from formic acid or from carbonic acid.

Representing now the simplest hydrocarbon, alcohol, aldehyde, and acid, by the structural formulas deduced from the facts, we have

$$C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right. \qquad C\left\{\begin{matrix}OH\\H\\H\\H\end{matrix}\right. \qquad C\left\{\begin{matrix}O\\H\\H\end{matrix}\right. \qquad C\left\{\begin{matrix}O\\OH.\\H\end{matrix}\right.$$

| Marsh gas. | Methyl alcohol. | Formic aldehyde. | Formic acid. |
|---|---|---|---|

Concerning the mechanism of the changes caused by oxidation, but little can be determined by experiment. We may regard methyl alcohol as the first and simplest product of oxidation of marsh gas. Starting with methyl alcohol, we might expect the next change to consist in the introduction of another oxygen atom, giving a body $C\left\{\begin{matrix}OH\\OH\\H\\H\end{matrix}\right.$. But it appears to be a law that, except under certain peculiar conditions, *one carbon atom* cannot hold two hydroxyls in combination, and that, if such a body is formed, it loses the elements of water; thus, $C\left\{\begin{matrix}OH\\OH\\H\\H\end{matrix}\right. = C\left\{\begin{matrix}O\\H\\H\end{matrix}\right. + H_2O$. The result would be the aldehyde. This kind of change is illustrated in the formation of carbon dioxide from the salts of carbonic acid. Instead of getting the acid $CO<^{OH}_{OH}$, which we would naturally expect, we get this minus water: —

$$CO<^{OH}_{OH} = CO_2 + H_2O.$$

Now, when the aldehyde is oxidized, another oxygen atom is introduced, and the substance thus produced is an acid, or the hydroxyl hydrogen can be replaced by metals, and has in general the characteristics of acid hydrogen. As soon as we have carbon in combination with oxygen as carbonyl, and also with hydroxyl, the substance containing the combination is an acid.

If, finally, the acid $C\left\{\begin{matrix}O\\OH\\H\end{matrix}\right.$ be oxidized, it is probable that the same change takes place as when the alcohol is oxidized. That is to say, the hydrogen is probably replaced by hydroxyl, when a compound containing two hydroxyls in combination with one carbon atom would be the result. This would be ordinary carbonic acid. But this breaks up into water and carbon dioxide, which, as we know, are the products of oxidation of formic acid.

All the many representatives of the great classes of carbon compounds known as the alcohols, aldehydes, and acids are closely related to the three fundamental substances, methyl alcohol, formic aldehyde, and formic acid. Replace one of the hydrogen atoms of methyl alcohol by a radical, and we get a new alcohol, which may be represented by the formula $C\left\{\begin{matrix}OH\\H\\H\\R\end{matrix}\right.$.

So also a similar replacement of a hydrogen atom in formic aldehyde gives another aldehyde, $C\left\{\begin{matrix}O\\H\\R\end{matrix}\right.$; and, finally, as we have seen, the acids of carbon may be represented by the formulas $C\left\{\begin{matrix}O\\OH\\R\end{matrix}\right.$, or R.CO.OH, or $CO<{R \atop OH}$, which show their relations to formic and carbonic acids. Hereafter, in writing the formulas of members of the three great classes, the structure will be represented by writing the hydroxyl group OH, the aldehyde group CHO, and the carboxyl group CO.OH or $CO_2H$, separately from the rest of the formula.

## 5. Ethereal Salts or Compound Ethers.

Whenever an acid acts upon an alcohol, the acid is neutralized either wholly or partly, and a product analogous to the salts is formed. Thus nitric acid and ethyl alcohol give ethyl nitrate: —

$$C_2H_5.OH + HNO_3 = C_2H_5.NO_3 + H_2O,$$

just as nitric acid and potassium hydroxide give potassium nitrate. It has been pointed out that the radicals, methyl, $CH_3$, and ethyl, $C_2H_5$, take the part of metals in the ethereal salts. We may thus get a series of methyl and ethyl salts with the various acids.

As regards the preparation of these compounds, it should be remarked that the action between an alcohol and an acid does not take place as readily as that between an acid and a metallic hydroxide. Only a few of the strongest acids act directly without aid. Such, for example, are nitric and sulphuric acids, though even the latter is not completely neutralized by action upon alcohols, as has already been seen in the preparation of ethyl-sulphuric acid, ${C_2H_5 \atop H}>SO_4$, for the purpose of making ether. Plainly ethyl-sulphuric acid is an acid ethereal salt, analogous to acid potassium sulphate. Both are still acid, though both are *likewise salts.*

The methods which may be used for preparing ethereal salts are the following: —

(1) Treatment of an acid with an alcohol. This is capable of only very limited application, as in the case of a few of the strongest acids.

(2) Treatment of the chloride of an acid with alcohol. This has been illustrated by the action of acetyl chloride, $C_2H_3O.Cl$, upon methyl alcohol (see p. 62): —

$$C_2H_3OCl + HO.CH_3 = C_2H_3O.OCH_3 + HCl,$$

or

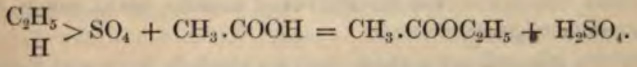
$$CH_3.COCl + HO.CH_3 = CH_3.COOCH_3 + HCl.$$

(3) Treatment of the silver salt of an acid with a halogen substitution-product of a hydrocarbon. For example, ethyl acetate may be made by treating silver acetate with brom-ethane: —

$$CH_3.COOAg + C_2H_5Br = CH_3COOC_2H_5 + AgBr.$$

This reaction is well adapted to showing the relation between the salt and the ethereal salt, and leaves no room for doubt that the two are strictly analogous.

(4) Treatment of a mixture of an alcohol and an acid with dry hydrochloric acid gas or strong sulphuric acid. The formation of ethyl acetate by this method was illustrated in Experiment 19, p. 60. The sulphuric acid facilitates the action by uniting with the alcohol to form ethyl-sulphuric acid, which with the acid gives the ethereal salt: —



$$\begin{matrix}C_2H_5\\H\end{matrix}\!>SO_4 + CH_3.COOH = CH_3.COOC_2H_5 + H_2SO_4.$$

The action of the hydrochloric acid is not understood. It is possible that it acts upon the acids forming the chloride, and that this then acts upon the alcohol, forming the ethereal salt: —

$$CH_3.COOH + HCl = CH_3.COCl + H_2O;$$

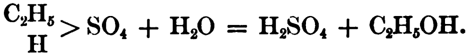
$$CH_3.COCl + C_2H_5OH = CH_3.COOC_2H_5 + HCl.$$

Among the more important ethereal salts of methyl and ethyl alcohols, the following may be mentioned: —

**Methyl-sulphuric acid,** $\begin{matrix}CH_3\\H\end{matrix}\!>SO_4$, formed by mixing methyl alcohol and sulphuric acid. The acid itself, as well as its salts, is very easily soluble in water.

**Ethyl nitrate,** $C_2H_5NO_3$, formed by treating alcohol with nitric acid. Unless precautions are taken in mixing these reagents, complete decomposition of the alcohol will take place, and the action will be accompanied by a violent explosion.

**Ethyl-sulphuric acid,** $\begin{matrix}C_2H_5\\H\end{matrix}\!>SO_4$. Made in the same way as the methyl compound. The acid and its salts are easily soluble in water. When boiled with water it is decomposed, yielding alcohol and sulphuric acid: —



$$\begin{matrix}C_2H_5\\H\end{matrix}\!>SO_4 + H_2O = H_2SO_4 + C_2H_5OH.$$

**Ethyl sulphate,** $(C_2H_5)_2SO_4$, is made by passing the vapor of sulphur trioxide into well-cooled ether: —

$$(C_2H_5)_2O + SO_3 = (C_2H_5)_2SO_4.$$

Phosphoric acid yields *ethyl phosphate*, $(C_2H_5)_3PO_4$, *di-ethyl-phosphoric acid*, $(C_2H_5)_2HPO_4$, and *ethyl-phosphoric acid*, $C_2H_5H_2PO_4$.

There also are similar derivatives of arsenic, boric, silicic, and other mineral acids.

Of the ethereal salts which the two alcohols form with formic and acetic acids, *methyl* and *ethyl acetates* are the best known. The methods of preparing them have already been considered. They are both liquids having pleasant odors. This is indeed a characteristic of many of the volatile ethereal salts of the acids of carbon, and many of the odors of fruits and flowers are due to the presence of one or another of these compounds. Many of them also are used for flavoring purposes instead of the natural substances.

**Experiment 22.** Make a mixture of 15 parts ($150^g$) of ordinary concentrated sulphuric acid and 6 parts ($60^g$) absolute alcohol. Add to it 10 parts ($100^g$) sodium acetate. Distil from a flask. Redistil the distillate. The ethyl acetate thus formed boils at 77°. What reactions take place in this case?

*Decomposition of ethereal salts.* Salts of most metals are decomposed when treated with an alkaline hydroxide, as caustic soda or caustic potash, the result being a salt of the alkali and the hydroxide of the replaced metal, as seen in the case of copper sulphate and sodium hydroxide: —

$$CuSO_4 + 2\,NaOH = Cu(OH)_2 + Na_2SO_4.$$

So also the ethereal salts are decomposed when treated with the alkalies, though, as a rule, not as readily as salts. It is usually necessary to boil the ethereal salt with the alkali when decomposition takes place, the radical, like the metal, appearing in the form of the hydroxide or alcohol, and the alkali metal taking its place. Thus, when ethyl sulphate is treated with a solution of caustic potash, this reaction takes place: —

$$(C_2H_5)_2SO_4 + 2\,KOH = K_2SO_4 + 2\,C_2H_5.OH;$$

and when ethyl acetate is treated with caustic soda, we have this reaction: —

$$CH_3.COOC_2H_5 + NaOH = CH_3.COONa + C_2H_5OH.$$

**Experiment 23.** In a $500^{cc}$ flask put $200^{cc}$ water, $50^g$ solid caustic potash, and $20^{cc}$ ethyl acetate. Connect with an inverted condenser, arranged as shown in Fig. 8. Boil gently for half an hour. Now connect the condenser with the flask for distilling, and again boil. Examine the distillate for alcohol. Acidify the contents of the flask with sulphuric acid, and again distil. What passes over?

All ethereal salts are decomposed by boiling with the caustic alkalies. As this decomposition is best known on the large scale in the preparation of soaps, it is commonly called saponification.

As will be shown, the fats are ethereal salts, and soap-making consists in decomposing these fats by means of the alkalies. Hence, generally, to *saponify* any ethereal salt means to decompose it by means of an alkali into the corresponding alcohol and the alkali salt of the acid contained in it.

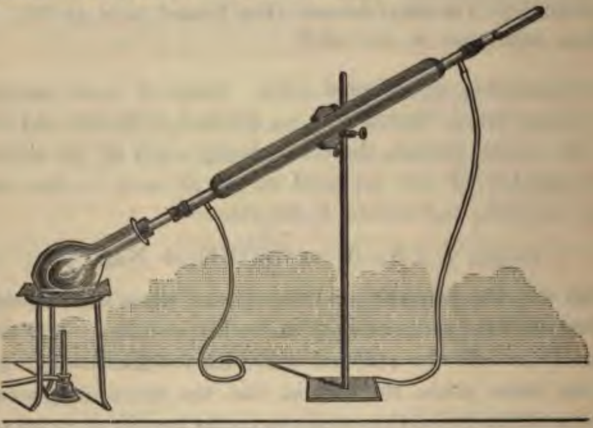


Fig. 8.

### 6. KETONES OR ACETONES.

When an acetate is distilled, a liquid passes over which has the composition $C_3H_6O$, and a carbonate remains behind. The reaction has been carefully studied, and has been shown to take place in accordance with the following equation: —

$$\begin{matrix} CH_3.COO \\ CH_3.COO \end{matrix} > Ca = C_3H_6O + CaCO_3.$$

The substance $C_3H_6O$ is known as *acetone*. It is the best known representative of a class of bodies which are sometimes called *acetones*, but more commonly *ketones*.

**Acetone, $C_3H_6O$.** — This substance has long been known as a product of the distillation of acetates, as above stated. It is contained in large quantities in the product obtained in the distillation of wood, and may be separated from the mixture after the removal of the acetic acid.

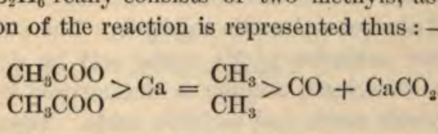
It may be purified by shaking a mixture containing it with a concentrated solution of mono-sodium sulphite. It unites with the salt, forming a compound analogous to that formed with aldehyde. The double compound may be separated, and when distilled with the addition of potassium carbonate acetone passes over.

Acetone is a colorless liquid having a penetrating pleasant ethereal odor. It boils at 56.3°. It is a good solvent for many carbon compounds, such as resins, fats, etc.

On studying the conduct of acetone, it soon becomes evident that it more closely resembles the aldehydes than any other bodies thus far considered. It is plainly not an acid nor an alcohol. It acts entirely different from either. It is not an ethereal salt, for on boiling with an alkali it does not yield an alcohol nor the salt of an acid. On the other hand, it unites with the acid sulphites like the aldehydes. Further, when treated with phosphorus pentachloride its oxygen is replaced by two chlorine atoms thus: —

$$C_3H_6O + PCl_5 = C_3H_6Cl_2 + POCl_3;$$

and when treated with nascent hydrogen, it is converted into a substance having alcoholic properties. These facts lead us to the conclusion that the substance contains carbonyl, CO, as the aldehydes do, and we thus have the formula, $C_2H_6CO$. The formation from calcium acetate leads further to the belief that the group $C_2H_6$ really consists of two methyls, as the simplest interpretation of the reaction is represented thus: —



$$\begin{matrix}CH_3COO\\CH_3COO\end{matrix}>Ca = \begin{matrix}CH_3\\CH_3\end{matrix}>CO + CaCO_3.$$

According to this, acetone is a compound of two methyl groups and carbonyl, or it is carbon monoxide whose two available affinities have been satisfied by two methyl groups.

We may test the correctness of this view by means of syntheses. If it is correct, it will be seen that acetone is closely related to acetyl chloride. It is acetyl chloride in which the chlorine has been replaced by methyl: —

| $CH_3.CO.Cl$ | $CH_3.CO.CH_3$. |
|---|---|
| Acetyl chloride. | Acetone. |

Now, when acetyl chloride is treated with zinc methyl, $Zn(CH_3)_2$, it yields acetone according to this equation: —

$$2\ CH_3.COCl + Zn(CH_3)_2 = 2\ CH_3.CO.CH_3 + ZnCl_2.$$

Further, acetone may be made by treating carbon monoxide with sodium methyl, a direct addition of two methyl groups to carbon monoxide being thus effected. The relation between acetone and ordinary acetic aldehyde is like that of an ethereal salt to its acid; that is, acetone is aldehyde, $CH_3.COH$, in which the hydrogen has been replaced by methyl, $CH_3.CO.CH_3$.

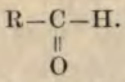
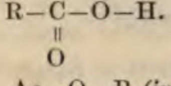
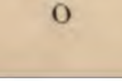
Like the aldehydes, the acetone has the power of taking up other substances, such as the acid sulphites, ammonia, hydrocyanic acid, hydrogen, etc. This power is in some way connected with the relation of the oxygen to the carbon, which is the same in both compounds. Nevertheless, this condition of the oxygen does not always carry with it the same power as seen in the case of the acids which also contain carbonyl.

By reduction with nascent hydrogen, acetone yields an alcohol of the formula $C_3H_8O$, known as *secondary propyl alcohol*, which when oxidized yields acetone. In other words, the relation between this alcohol and acetone is much the same as that between ethyl alcohol and acetic aldehyde. But while the aldehyde by further oxidation yields acetic acid by simply taking up one atom of oxygen, acetone is decomposed by oxidizing agents, and yields acetic and carbonic acids. Towards oxidizing agents, then, acetones (for it will be shown that other acetones conduct themselves in the same way) act entirely differently from the aldehydes. The alcohol above mentioned as related to acetone is the simplest representative of a class of alcohols differing in some respects from the substances commonly called alcohols.

---

We have thus considered the most important representatives of six classes of oxygen derivatives of the hydrocarbons, and, by a study of their chemical conduct and the methods available for their preparation, have formed views in regard to the relations between them. In our ordinary language we may express these relations briefly thus: The alcohols are the hydroxyl derivatives of the hydrocarbons or the hydroxides of certain groups called *radicals;* the ethers are the oxides of these same radicals; the aldehydes are compounds consisting of carbonyl, hydrogen, and a radical; the acids are compounds of carbonyl, hydroxyl, and a radical, or, better, they are carbonic acid in which hydrogen and oxygen, or hydroxyl, have been replaced by a radical; the ethereal salts are compounds like ordinary metallic salts, only they contain a radical in the place of the metal; and, finally, the ketones are aldehydes in which the distinctively aldehyde hydrogen has been replaced by a radical, or they are compounds consisting of carbonyl and two radicals.

These ideas are expressed in formulas thus, R being any univalent radical like methyl, $CH_3$, or ethyl, $C_2H_5$: —

Alcohol . . . . $\mathrm{R-O-H}$.
Ether . . . . . $\mathrm{R-O-R}$.
Aldehyde . . . .

$\mathrm{R-\underset{\underset{\textstyle O}{\|}}{C}-H}$.
Acid . . . . . .

$\mathrm{R-\underset{\underset{\textstyle O}{\|}}{C}-O-H}$.
Ethereal salt . . $\mathrm{Ac-O-R}$ (in which $\mathrm{Ac-O-H}$ represents any monobasic acid).
Ketone . . . .

$\mathrm{R-\underset{\underset{\textstyle O}{\|}}{C}-R}$.

# CHAPTER V.

## SULPHUR DERIVATIVES OF METHANE AND ETHANE.

### 1. MERCAPTANS.

THE simplest derivatives of methane and ethane containing sulphur are the so-called *mercaptans* or *sulphur alcohols*. They may be made by a method similar to one described under the head of Alcohols. When a mono-halogen derivative of a hydrocarbon, as brom-methane, $CH_3Br$, is treated with the hydroxide of a metal, as silver hydroxide, $AgOH$, an alcohol is formed:—

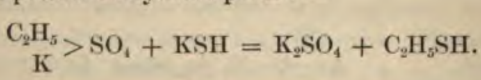
$$CH_3Br + AgOH = CH_3OH + AgBr.$$

So, also, when a similar halogen derivative is treated with a *hydrosulphide* instead of a *hydroxide*, a compound is obtained which we may regard as an alcohol in which the oxygen has been replaced by sulphur:—

$$CH_3Br + KSH = CH_3SH + KBr.$$

The compound is called a *mercaptan*.

**Ethyl-mercaptan, $C_2H_5.SH$.**—This substance may be prepared by treating iodo-ethane, $C_2H_5I$, with an alcoholic solution of potassium hydrosulphide, $KSH$; also by distilling a mixture of the concentrated solutions of potassium ethylsulphate and potassium hydrosulphide:—



$$\begin{matrix} C_2H_5 \\ K \end{matrix} > SO_4 + KSH = K_2SO_4 + C_2H_5SH.$$

It is a liquid of an *extremely disagreeable odor;* it boils at 37°; *and is difficultly* soluble in water.

The name "mercaptan" was given to it on account of its action towards mercury. It readily forms a compound in which mercury takes the place of hydrogen, $(C_2H_5S)_2Hg$. The name refers to its power of seizing mercury (*mercurius* and *captans*). It forms many other well-characterized metallic derivatives like this mercury compound.

When the sodium compound of mercaptan is exposed to the air, it takes up oxygen. So, also, when mercaptan itself is treated with nitric acid, it is oxidized, the product having the formula $C_2H_5 . SO_3H$. It will thus be seen that, though in composition mercaptan is analogous to alcohol, towards oxidizing agents it conducts itself quite differently. In the case of alcohol two atoms of hydrogen are replaced by one of oxygen. In the case of mercaptan three atoms of oxygen are added directly to the molecule. It will be shown that this new acid, which is called *ethyl-sulphonic acid*, bears to sulphuric acid a relation similar to that which acetic acid bears to carbonic acid; and that it bears to sulphurous acid a relation similar to that which acetic acid bears to formic acid.

When treated with phosphorus pentachloride it yields a chloride, $C_2H_5 . SO_2Cl$; and, when this is treated with nascent hydrogen (zinc and hydrochloric acid), it is reduced to mercaptan: —

$$C_2H_5 . SO_2Cl + 6\,H = C_2H_5 . SH + HCl + 2\,H_2O.$$

## 2. Sulphur Ethers.

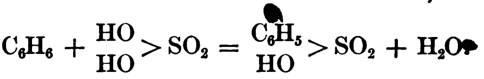
There are compounds known similar to the ethers, containing sulphur in the place of the oxygen of the ethers. Such are methyl-sulphide, $(CH_3)_2S$, and ethyl-sulphide, $(C_2H_5)_2S$. These are made by treating brom- or iodo-methane or ethane with potassium sulphide: —

$$2\,C_2H_5I + K_2S = (C_2H_5)_2S + 2\,KI.$$

They are liquids of very disagreeable odors.

### 3. Sulphonic Acids.

It was stated above, that when mercaptan is oxidized it is converted into an acid of the formula $C_2H_5.SO_3H$, or *ethyl-sulphonic acid.* This is the representative of a large class of bodies which are commonly made by treating carbon compounds with sulphuric acid. These sulphonic acids can best be studied in connection with another series of hydrocarbons. Under the head of Benzene (which see) it will be shown that, when this hydrocarbon is treated with sulphuric acid, a reaction takes place which may be represented thus:—

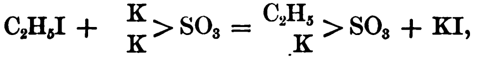


$$C_6H_6 + \begin{matrix}HO\\HO\end{matrix}>SO_2 = \begin{matrix}C_6H_5\\HO\end{matrix}>SO_2 + H_2O$$

**Benzene.** **Benzene-sulphonic acid.**

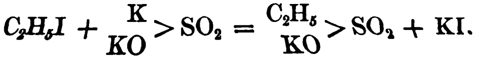
The sulphonic acid thus obtained may also be made by oxidizing the corresponding mercaptan or hydrosulphide, $C_6H_5.SH$. Accordingly, the sulphonic acid appears to be sulphuric acid in which a hydroxyl has been replaced by the radical $C_6H_5$. Reasoning by analogy, which, fortunately, is supported by other arguments, we may conclude that ethyl-sulphonic acid formed from ethyl-mercaptan bears a similar relation to sulphuric acid, and corresponds to the formula $\begin{matrix}C_2H_5\\HO\end{matrix}>SO_2$. So, also, methyl-sulphonic acid obtained by oxidation of methyl-mercaptan should be represented by the formula $\begin{matrix}CH_3\\HO\end{matrix}>SO_2$ or $CH_3.SO_2OH$. *Its relation to sulphuric acid is the same as that of acetic acid to carbonic acid.*

Another method by which the sulphonic acids may be prepared consists in treating a sulphite with a halogen substitution-product. Thus ethyl-sulphonic acid may be prepared from potassium sulphite and iodo-ethane:—



$$C_2H_5I + \begin{matrix}K\\K\end{matrix}>SO_3 = \begin{matrix}C_2H_5\\K\end{matrix}>SO_3 + KI,$$

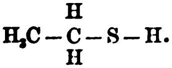
*or*



$$C_2H_5I + \begin{matrix}K\\KO\end{matrix}>SO_2 = \begin{matrix}C_2H_5\\KO\end{matrix}>SO_2 + KI.$$

According to this reaction the sulphonic acids would appear to be identical with the ethereal salts of sulphurous acid, but they do not conduct themselves like ethereal salts. The difference is particularly noticeable in connection with the stability, the sulphonic acids as a class being much more stable than the ethereal salts as a class. At present it would be somewhat premature to discuss fully the question as to their relations. Whatever we may call them, they are closely related to sulphurous acid, and are derived from it by replacement of hydrogen by a radical, just as acetic acid may be regarded as derived from formic acid by replacement of hydrogen by a radical. These relations may be represented by the following formulas: —

| | | | |
|---|---|---|---|
| Carbonic acid, | $CO < \begin{matrix} OH \\ OH \end{matrix}.$ | Sulphuric acid, | $SO_2 < \begin{matrix} OH \\ OH \end{matrix}.$ |
| Formic acid, | $CO < \begin{matrix} H \\ OH \end{matrix}.$ | Sulphurous acid, | $SO_2 < \begin{matrix} H \\ OH \end{matrix}.$ |
| Acetic acid, | $CO < \begin{matrix} CH_3 \\ OH \end{matrix}.$ | Methyl-sulphonic acid, | $SO_2 < \begin{matrix} CH_3 \\ OH \end{matrix}.$ |
| Any carbonic acid, | $CO < \begin{matrix} R \\ OH \end{matrix}.$ | Any sulphonic acid, | $SO_2 < \begin{matrix} R \\ OH \end{matrix}.$ |

The difference between a sulphonic acid and an ethereal salt of sulphuric acid should be specially noticed. Compare for this purpose ethyl-sulphuric acid, $\begin{matrix} C_2H_5O \\ HO \end{matrix} > SO_2$, and ethyl-sulphonic acid, $\begin{matrix} C_2H_5 \\ HO \end{matrix} > SO_2$. Both are monobasic acids, and both contain ethyl, but there is a difference of one atom of oxygen in their composition. The reactions of the substances are such as to lead to the conclusion that in ethyl-sulphonic acid the ethyl group is directly connected with the sulphur; whereas, that in ethyl-sulphuric acid the connection is established by means of oxygen. The strongest argument in favor of this view is perhaps that which is founded on the formation of the sulphonic acids by oxidation of the hydrosulphides or mercaptans. It can hardly be doubted that in ethyl mercaptan the sulphur is in direct combination with the ethyl; or, to go still farther, that it is in combination with carbon as represented in the formula  $H_3C-\overset{H}{\underset{H}{C}}-S-H$. Now, by oxidation of mercaptan, three atoms of oxygen are added, and the simplest view we can take of the reaction is that the sulphur is left undisturbed in its relations to ethyl, but that it has taken up the oxygen, as represented in the formula $C_2H_5-SO_2.OH$. As has been shown, the oxygen can be removed again by nascent hydrogen, and the result is mercaptan. The study of the sulphonic acids in their relations to sulphuric and sulphurous acids has been of considerable assistance in enabling chemists to form conceptions in regard to the relations of the constituents of the two latter. The view which is forced upon us by a consideration of the reactions described above is that sulphurous acid differs from sulphuric acid in containing a hydrogen atom in place of hydroxyl, as represented in the formulas $SO_2<\begin{matrix}OH\\OH\end{matrix}$ and $SO_2<\begin{matrix}H\\OH\end{matrix}$; and, further, that in sulphurous acid one hydrogen is in combination with sulphur and the other with oxygen.

# CHAPTER VI.

## NITROGEN DERIVATIVES OF METHANE AND ETHANE.

THE simplest compounds of carbon containing nitrogen are cyanogen and hydrocyanic acid. Strictly speaking, neither can be regarded as a derivative of a hydrocarbon, unless indeed we consider hydrocyanic acid as marsh gas, in which three hydrogen atoms have been replaced by one nitrogen: $C\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right.$ and $C\left\{\begin{matrix}N\\H\end{matrix}\right.$. That, however, is a mere matter of words, as there is nothing in the conduct of either substance, or in the methods of formation of hydrocyanic acid, that would lead us to suspect any relation between them. Though cyanogen and hydrocyanic acid are therefore not to be considered as derivatives of the hydrocarbons, they form the starting-point for the preparation of so many important compounds that they and their simpler derivatives must receive some consideration at this stage.

**Cyanogen, $(CN)_2$.** — All organic compounds which contain nitrogen give sodium cyanide when ignited with sodium. So, also, potassium cyanide is formed when charcoal containing nitrogen is heated with potassium carbonate. Cyanogen itself is most readily made by heating mercuric cyanide, $Hg(CN)_2$. The decomposition which takes place is, in the main, like the simple decomposition of mercuric oxide in preparing oxygen: —

$$\begin{aligned} Hg(CN)_2 &= Hg + (CN)_2; \\ HgO &= Hg + O. \end{aligned}$$

But, in heating mercuric cyanide, a black solid substance, *paracyanogen*, is formed, and remains behind in the retort. It has the same composition as cyanogen, and is therefore a polymeric modification.

Cyanogen (from *κύανος*, *blue*) owes its name to the fact that several of its compounds have a blue color. It is a colorless gas, which is easily soluble in water and alcohol, and *is extremely poisonous*. It burns with a purple-colored flame.

In aqueous solution, cyanogen soon undergoes change, and a brown amorphous body is deposited. In the solution are found hydrocyanic acid, oxalic acid, ammonia, and carbon dioxide. A little dilute acid prevents this decomposition.

**Hydrocyanic acid, HCN.** — This acid, which is commonly known by the name of *prussic acid*, occurs in nature in amygdalin, in combination with other substances, in bitter almonds, the leaves of the cherry, laurel, etc. It is prepared by decomposing metallic cyanides with hydrochloric acid, as represented in the equation: —

$$KCN + HCl = KCl + HCN.$$

It may also be made by treating chloroform with ammonia: —

$$CHCl_3 + NH_3 = HCN + 3\,HCl,$$

or

$$CHCl_3 + 5\,NH_3 = NH_4.CN + 3\,NH_4Cl.$$

It is a volatile liquid, boiling at 26.5°, which solidifies at $-15°$. It has a very characteristic odor, suggesting bitter almonds. *It is extremely poisonous.* It dissolves in water in all proportions, and it is such a solution which is known as prussic acid. Pure hydrocyanic acid is very unstable. By standing, a brown body is deposited. By boiling with alkalies or acids, it is converted into formic acid and ammonia (see p. 56).

Hydrocyanic acid may be detected by the fact that when its solution is saturated with caustic potash, and a solution containing a ferrous and a ferric salt added, a precipitate of Prussian blue is formed; or, by adding yellow ammonium sulphide to its solution, evaporating off the excess of ammonium sulphide, and then adding a drop of solution of ferric chloride. If hydrocyanic acid was present, the solution turns a deep blood red.

**Cyanides.** — Hydrocyanic, like hydrochloric acid, forms a series of salts. They are called the *cyanides*. The cyanides of the alkali metals and of mercury are soluble in water. The cyanides of the heavy metals have a marked tendency to form double cyanides, and those double cyanides which contain an alkali metal are soluble in water. Hence, the precipitates formed by potassium cyanide, in solutions containing the heavy metals, are dissolved by excess of the cyanide.

Among the best known double cyanides are the two salts, *potassium ferrocyanide* and *potassium ferricyanide*. The former is commonly known as *yellow prussiate of potash*, and the latter as *red prussiate of potash*.

**Potassium ferrocyanide, $(4\,KCN)Fe(CN)_2 + 3\,H_2O$.** — This salt is made on the large scale by melting together, in iron vessels, refuse animal substances (*i.e.*, organic matter containing nitrogen) with potassium carbonate and iron. The mass is treated with water, and the salt which is thus extracted purified by crystallization.

It crystallizes in large yellow crystals, and is soluble in about four parts of water at 15°.

When ignited, it breaks up according to this equation: —

$$4\,KCN.Fe(CN)_2 = 4\,KCN + FeC_2 + N_2.$$

This decomposition is made use of for the purpose of preparing potassium cyanide. As, however, a portion of the cyanogen is lost in this way, potassium carbonate is generally added, when the reaction represented by the following equation takes place: —

$$4\,KCN.Fe(CN)_2 + K_2CO_3 = 5\,KCN + KCNO + CO_2 + Fe.$$

The *potassium cyanide* made in this way always necessarily contains potassium cyanate, KCNO.

**Experiment 24.**[1] Make a mixture of 8 parts (160g) dehydrated potassium ferrocyanide and 3 parts (60g) dry potassium carbonate. Fuse in an iron crucible, at a low red heat, until a specimen taken out and placed on a stone is white when solid. Then pour out on a flat, smooth stone, and afterwards break up and put in a dry bottle.

When treated with dilute sulphuric acid, the ferrocyanide yields hydrocyanic acid thus: —

$$\begin{aligned} &2\,[4\,\mathrm{KCN.Fe(CN)_2}] + 3\,\mathrm{H_2SO_4} \\ &\quad = 6\,\mathrm{HCN} + 2\,[\mathrm{KCN.Fe(CN)_2}] + 3\,\mathrm{K_2SO_4}. \end{aligned}$$

This reaction is the one actually made use of for the preparation of hydrocyanic acid.

Potassium ferrocyanide is the starting-point for the preparation of all compounds containing cyanogen.

**Potassium ferricyanide, $3\,\mathrm{KCN.Fe(CN)_3}$.** — This salt, known as red prussiate of potash, is prepared *by oxidizing the ferrocyanide.* The oxidation is effected most readily by means of chlorine.

**Experiment 25.** Pass chlorine into a solution of potassium ferrocyanide until the solution ceases to give a precipitate with ferric chloride. Then evaporate to crystallization.

Other oxidizing agents, such as bromine, potassium permanganate, lead peroxide, etc., effect the same transformation. The essential part of the change is that of the ferrous cyanide, $\mathrm{Fe(CN)_2}$, in the ferrocyanide, to ferric cyanide, $\mathrm{Fe(CN)_3}$, which is in the ferricyanide. Potassium ferricyanide is easily soluble in water, and crystallizes from its concentrated solutions in large, dark-red crystals belonging to the rhombic system.

In alkaline solutions it is an excellent oxidizing agent.

---

[1] Experiments 24 and 26 may be postponed until urea is considered, when they may be combined with the artificial preparation of urea.

Reducing agents, such as hydrogen sulphide, sodium thiosulphate (hyposulphite), etc., convert it into the yellow salt.

*Prussian blue*, *Turnbull's blue*, *soluble Prussian blue*, and *Berlin green* are complex cyanides of iron represented by the formulas

$$4\,Fe(CN)_3 . 3\,Fe(CN)_2,$$
$$3\,Fe(CN)_2 . 2\,Fe(CN)_3,$$
$$KCN . Fe(CN)_3 . Fe(CN)_2,$$

and $Fe_3(CN)_8 + 4\,H_2O$, respectively.

For a full account of the many compounds of the metals and cyanogen, the student is referred to larger works.

**Cyanogen chlorides.** — When chlorine is allowed to act upon cyanides or dilute hydrocyanic acid, a volatile liquid is formed which has the composition represented by the formula $CNCl$. It boils at 15.5°, and its vapor acts upon the eyes, causing tears. It is known as *liquid cyanogen chloride* to distinguish it from *solid cyanogen chloride*. The latter has the formula $(CN)_3Cl_3$, and is formed by treating anhydrous hydrocyanic acid with chlorine in direct sunlight. The liquid variety is partially transformed into the solid when kept in sealed tubes.

Similar compounds of cyanogen with bromine and iodine are known.

**Cyanic acid, CONH.** — When a cyanide of an alkali is treated with an oxidizing agent, it takes up oxygen and is converted into a cyanate: —

$$CNK + O = CONK.$$

**Experiment 26.**[1] Heat a mixture of 8 parts ($160^g$) dehydrated potassium ferrocyanide, and 3 parts ($60^g$) dry potassium carbonate in an iron crucible. When the transformation into the cyanide is complete (see Ex. 24, p. 82), take the crucible out of the furnace; and, after it has cooled down somewhat, but while the mass is still liquid, add gradually 15 parts (300$^g$) red lead, stirring during the operation. Put the crucible again in the furnace for a little while; allow the reduced lead to settle, and then pour out the contents on a smooth stone. After the mass is cold, break up and extract the cyanate with alcohol (of 86 per cent).

---

[1] See Note, p. 82.

Cyanic acid cannot be separated from its salts, as it breaks up with water into ammonia and carbon dioxide: —

$$CONH + H_2O = NH_3 + CO_2.$$

The potassium salt is easily soluble in water, but is easily decomposed by it, yielding ammonia and potassium carbonate: —

$$CONK + 2\,H_2O = KHCO_3 + NH_3.$$

The most interesting salt of cyanic acid is *ammonium cyanate*, $CON.NH_4$. It may be made by adding ammonium sulphate to a solution of the potassium salt. It is easily soluble in water; but, if allowed to stand in solution, or if its solution be heated, *it is completely transformed into urea*, which is isomeric with it. The interest connected with this transformation was referred to in the introductory chapter (p. 1). It will be considered more fully under the head of urea.

**Cyanuric acid, $C_3N_3H_3O_3$.** — This acid bears a relation to cyanic acid similar to that which solid cyanogen chloride, $(CN)_3Cl_3$, bears to the liquid variety. It is made by treating the solid chloride with water, and also by heating urea. It is a crystallized substance.

**Sulpho-cyanic acid, CNSH.** — Just as the cyanides of the alkalies take up oxygen and are converted into cyanates, so also they take up sulphur and are converted into sulpho-cyanates: —

$$CNK + S = \underset{\text{Potassium sulpho-cyanate.}}{CNSK.}$$

**Experiment 27.** Melt together in an iron crucible 17 parts (85g) dry potassium carbonate and 32 parts (160g) sulphur, and then add 46 parts (230g) powdered dehydrated potassium ferrocyanide. Keep the mass at a low red heat until the ferrocyanide is destroyed. After cooling, extract with water, neutralize the filtered solution with sulphuric acid, evaporate, and separate from potassium sulphate by means of alcohol.

*Potassium sulpho-cyanate* crystallizes in long striated prisms without water of crystallization. It is deliquescent. When dissolved in water the temperature sinks markedly. When 100 parts of water of 10.8° are mixed with 150 parts of the salt, the temperature sinks to $-23.7°$. By evaporation of the solution, the salt can be recovered.

**Experiment 28.** Dissolve some potassium sulpho-cyanate in water, and note the temperature before and after introducing the salt.

*Ammonium sulpho-cyanate*, $CNS.NH_4$. This salt is most easily prepared by treating carbon bisulphide with a solution of ammonia in dilute alcohol:—

$$CS_2 + 4\,NH_3 = CNS.NH_4 + (NH_4)_2S.$$

**Experiment 29.** Mix 240cc strong aqueous ammonia, 240cc alcohol, and 60g carbon bisulphide. Allow the mixture to stand for one or more days. Then distil down to one-third of the original volume, and filter while still hot the solution left in the flask. On cooling, ammonium sulpho-cyanate will crystallize out.

The salt crystallizes in plates. It melts at 147° (try it), and at 170° it is transformed into the isomeric substance known as sulpho-urea. (Analogy to transformation of ammonium cyanate.)

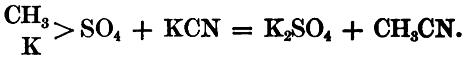
---

Having thus considered some of the more important simpler cyanogen compounds, we may now return to the nitrogen derivatives of the hydrocarbons. For convenience, these may be divided into three classes:—

(1) *Those which are related to cyanogen;*
(2) *Those which are related to ammonia;*
(3) *Those which are related to nitric acid.*

## CYANIDES.

**Methyl cyanide, $CH_3.CN$.**—This compound is formed by distilling a mixture of potassium methyl-sulphate and potassium cyanide:—



$$\begin{matrix} CH_3 \\ K \end{matrix}\!\!> SO_4 + KCN = K_2SO_4 + CH_3CN.$$

It is a liquid boiling at 82°.

According to the method of preparation, it must be regarded as an ethereal salt of hydrocyanic acid, containing methyl in the place of the potassium of the potassium salt.

**Ethyl cyanide, $C_2H_5.CN$.**—Formed like the methyl compound. Also by heating chlor-ethane with potassium cyanide:—

$$C_2H_5Cl + KCN = C_2H_5.CN + KCl.$$

It is a liquid boiling at 98°.

The two most characteristic reactions of these cyanides are (1) that which is effected by caustic alkalies, and (2) that effected by nascent hydrogen.

When methyl cyanide is treated with caustic potash, it yields acetic acid and ammonia:—

$$CH_3.CN + H_2O + KOH = CH_3.CO_2K + NH_3.$$

This reaction is strictly analogous to that which takes place with hydrocyanic acid yielding formic acid (see p. 56). In the same way ethyl cyanide yields an acid of the formula $C_3H_6O_2$ (or $C_2H_5.CO_2H$). Thus, by making a cyanide, we have it in our power to make an acid containing the same number of carbon atoms.

This reaction, therefore, enables us to pass from an alcohol to an acid containing one atom of carbon more than the alcohol contains. It has been of great service in the study of the compounds of carbon.

**Note for Student.** — Show how, by starting with methyl-alcohol, acetic acid may be made by passing through the cyanide.

There are two ways in which we may consider the cyanogen group linked to methyl in methyl cyanide; viz., either by the carbon atom, as represented in the formula $H_3C-C-N$, or by the nitrogen atom, as represented thus, $H_3C-N-C$. The ease with which the nitrogen is separated from the compound, leaving the two carbon atoms together, as shown in the reaction with caustic potash, naturally leads to the conclusion that the former view is the correct one. If it is correct, it would appear to follow that in potassium cyanide the potassium is in combination with carbon as represented in the formula $K-C-N$, and further that in hydrocyanic acid the hydrogen is in combination with carbon, as shown thus, $H-C-N$.

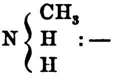
In consequence of the close relation existing between the cyanides and the acids, the former are frequently spoken of as the *nitriles* of the acids. Thus methyl cyanide, which is converted into acetic acid by boiling with caustic potash, is called the nitrile of acetic acid, or aceto-nitrile. In the same way hydrocyanic acid itself may be regarded as the nitrile of formic acid, or formo-nitrile.

When methyl cyanide is treated with nascent hydrogen, it is converted into a substance which closely resembles ammonia, and is known as *ethyl-amine*. It will be shown to bear to ammonia the relation indicated by the formula $N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right.$; *i.e.*, it is ammonia in which one hydrogen has been replaced by ethyl. The reaction may be represented by the equation: —

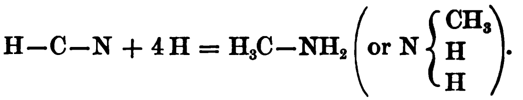
$$H_3C-C-N + 4\,H = H_3C-H_2C-NH_2\left(\text{or } N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right.\right).$$

This transformation strengthens the conclusion already reached, that the two carbon atoms in methyl cyanide are directly united. If this were not the case, it is difficult to see how a compound containing ethyl in which the two carbon atoms are unquestionably united, could be formed so easily from it.

Just as methyl cyanide yields ethyl-amine when treated with nascent hydrogen, so hydrocyanic acid yields methyl-amine



$N\left\{\begin{array}{l}CH_3\\H\\H\end{array}\right.$ :—



$$H-C-N + 4H = H_3C-NH_2\left(\text{or } N\left\{\begin{array}{l}CH_3\\H\\H\end{array}\right.\right).$$

The amines, or substituted ammonias, will be considered more fully hereafter.

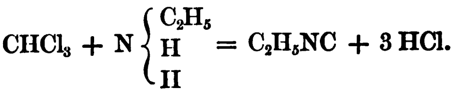
### Isocyanides or Carbamines.

If, in making an ethereal salt of hydrocyanic acid from a salt, the silver salt be used, a compound is obtained having the same composition as the cyanide, but differing very markedly from it. The substance thus obtained is called an *isocyanide* or *carbamine.*

**Ethyl isocyanide or ethyl carbamine, $C_2H_5.NC$.**—This compound is obtained when silver cyanide and iodo-ethane are heated together:—

$$C_2H_5I + AgNC = C_2H_5NC + AgI.$$

It is also formed when chloroform and ethyl-amine (see above) are brought together:—



$$CHCl_3 + N\left\{\begin{array}{l}C_2H_5\\H\\H\end{array}\right. = C_2H_5NC + 3\,HCl.$$

It is a liquid boiling at 79°. It is characterized by an *unbearable, indescribable odor.* The methyl compound obtained by the same method boils at 58° to 59°, but otherwise has properties almost identical with those of ethyl isocyanide.

The reactions of these substances are quite different from those of the cyanides. They are decomposed only with great difficulty by the caustic alkalies; but, when brought together with hydrochloric acid, they undergo an interesting change, which may be represented by the following equation for the methyl compound:—

$$CH_3.NC + 2\,H_2O = \underset{\text{Methyl-amine.}}{CH_3{-}NH_2} + \underset{\text{Formic acid.}}{H.CO_2H.}$$

This reaction indicates that in the isocyanides the cyanogen group is united to the radical by means of nitrogen, as represented by the formula $H_3C{-}N{-}C$. Hence it is, in all probability, that when they undergo decomposition the nitrogen remains in combination with the radical, while the carbon of the cyanogen group passes out of the compound. The conduct of ethyl isocyanide is represented by the equation:—

$$C_2H_5.NC + 2\,H_2O = C_2H_5{-}NH_2 + H.CO_2H.$$

The reactions of the cyanides and of the isocyanides, and the conclusions drawn from them, admirably illustrate the methods used in determining the structure of compounds of carbon; and they are specially valuable, as the connection between the facts and the conclusions, as expressed in the formulas, can be traced so clearly.

The fact, that the silver salt of hydrocyanic acid yields isocyanides, while the potassium and other salts yield cyanides with the halogen derivatives of the hydrocarbons, leads us to suspect that in silver cyanide the metal may be in combination with nitrogen and not with carbon. There are other facts known which indicate a tendency on the part of silver to unite with nitrogen in carbon compounds. It would lead too far to discuss this subject here.

It seems possible that isomeric salts of cyanogen may be discovered corresponding to the cyanides of the radicals and to the isocyanides. There is no fact known which makes the existence of two potassium cyanides and two silver cyanides seem improbable. The two series of salts would be derivatives of hydrocyanic acid, $H-C-N$, and isohydrocyanic acid, $H-N-C$.

**Experiment 30.** The odor of the isocyanides, as has been stated, is extremely disagreeable, and in concentrated form it is unbearable. A vivid impression in regard to this property may be produced by the following experiment. In a test-tube bring together a *little* chloroform, aniline, and alcoholic potash. The reaction takes place at once. It is better to perform the experiment out-of-doors, and in such a place that the tube with its contents can be thrown away without molesting any one. The aniline used is a substituted ammonia analogous to methylamine, containing the radical $C_6H_5$ in place of methyl. The isocyanide formed has the formula $C_6H_5.NC$.

## CYANATES AND ISOCYANATES.

There are two series of compounds bearing to cyanic acid much the same relation as that which the cyanides and isocyanides bear to hydrocyanic acid.

In the *cyanates*, which are made by passing cyanogen chloride into the alcohols ($CH_3OH + CNCl = CH_3OCN + HCl$), the radical is believed to be united to the cyanogen group by means of oxygen, as represented in the formula $CH_3-O-CN$.

In the isocyanates (first called *cyanates*), on the other hand, the radical is believed to be united to the cyanogen by means of nitrogen, as represented thus, $CH_3-N-CO$. The isocyanates are made by distilling potassium cyanate with the potassium salt of methyl- or ethyl-sulphuric acid. They may be made also by bringing together the iodides of radicals, as iodo-methane and silver cyanate. They are very volatile substances, which have penetrating and suffocating odors.

One of the principal reactions of the cyanates is that which they undergo with caustic alkalies, hydrochloric acid, etc. They yield cyanic acid, and a compound containing the radical which they contained.

The isocyanates readily yield substituted ammonias, just as the isocyanides do:—

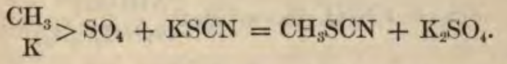
$$C_2H_5-N-CO + H_2O = C_2H_5.NH_2 + CO_2;$$
$$CH_3-N-CO + H_2O = CH_3.NH_2 + CO_2.$$

The views held in regard to the structure of the cyanates and isocyanates are based upon these reactions, which, as will be observed, are very similar to those more fully considered in discussing the difference between the cyanides and isocyanides.

The existence of two cyanic acids, and of two series of salts derived from them, seems probable.

### SULPHO-CYANATES.

The ethereal salts of sulphocyanic acid are easily made by distilling potassium sulphocyanate and the potassium salt of methyl- or ethyl-sulphuric acid:—



$$\begin{matrix} CH_3 \\ K \end{matrix} > SO_4 + KSCN = CH_3SCN + K_2SO_4.$$

The ethyl compound, which is very similar to the methyl compound, is a liquid boiling at 146°.

When boiled with nitric acid, it is oxidized to ethyl-sulphonic acid. Now, it has been shown above (see p. 77), that in ethyl-sulphonic acid the ethyl in all probability is in combination with the sulphur. It hence follows that, in the sulphocyanates obtained from potassium sulphocyanate, the radical is also in combination with sulphur, as indicated in the formula, $C_2H_5-S-CN$. This view is supported by the fact that ethyl sulpho-cyanate readily yields ethyl sulphide as a product of decomposition.

### ISO-SULPHO-CYANATES OR MUSTARD-OILS.

A number of compounds are known isomeric with the sulpho-cyanates. The best-known member of the class is ordinary *mustard-oil*. Hence they have been called mustard-oils, and they are known most frequently by this name. The mustard-oils are made by means of a series of somewhat complicated reactions, which it is rather difficult to interpret without a comparison with some similar reactions which take place between simpler substances.

When dry ammonia and dry carbon dioxide act upon each other, so-called anhydrous ammonium carbonate is formed. This is really the ammonium salt of carbamic acid, $CO<\begin{matrix}NH_2\\OH\end{matrix}$. Its formation is represented thus: —

$$CO_2 + 2\,NH_3 = CO<\begin{matrix}NH_2\\ONH_4\end{matrix}.$$

Now, remembering that carbon bisulphide is similar to carbon dioxide, and that ethyl-amine is similar to ammonia, we can readily understand the reaction which takes place when these two substances are brought together: —

$$CS_2 + 2\,NH_2C_2H_5 = CS<\begin{matrix}NHC_2H_5\\S(NH_3C_2H_5)\end{matrix}.$$

The product formed is the ethyl-ammonium salt of the acid $CS<\begin{matrix}NHC_2H_5\\SH\end{matrix}$, which may be called ethyl-sulpho-carbamic acid. When the ethyl-ammonium salt is treated with silver nitrate, the corresponding silver salt, $CS<\begin{matrix}NHC_2H_5\\SAg\end{matrix}$, is precipitated. And finally, when this salt is distilled, it breaks up, yielding *ethyl mustard-oil*, silver sulphide, and hydrogen sulphide: —

$$2\,CS<\begin{matrix}NHC_2H_5\\SAg\end{matrix} = 2\,SC{-}NC_2H_5 + H_2S + Ag_2S.$$

Ethyl mustard-oil is an oily liquid which does not mix with water. It has a very penetrating odor, and acts upon the mucous membranes of the eyes and nose in the same way as ordinary oil of mustard. The properties of the two are so much alike that one could be substituted for the other.

Some of the arguments have been stated which lead to the view that in the sulpho-cyanates the radical is in combination with sulphur. Having once accepted this view, we would naturally suspect that in the mustard-oils the radical is in combination with nitrogen, and the question arises whether the reactions of these bodies are of such a character as to justify this suspicion? They certainly are. In the first place, when heated with water or with hydrochloric acid, ethyl mustard-oil is decomposed, yielding *ethyl-amine*, carbon dioxide, and hydrogen sulphide: —

$$SC-NC_2H_5 + 2\,H_2O = C_2H_5.NH_2 + H_2S + CO_2.$$

And, in the second place, nascent hydrogen converts it into *ethyl-amine* and formic thioaldehyde (*i.e.*, formic aldehyde in which the oxygen has been replaced by sulphur): —

$$SC-NC_2H_5 + 4\,H = C_2H_5.NH_2 + H_2CS.$$

Thus, as will be seen, the tendency of the sulpho-cyanates is to yield sulphides of the radicals like ethyl sulphide, $(C_2H_5)_2S$; the tendency of the iso-sulpho-cyanates is to yield substituted ammonias, like ethyl-amine $NH_2.C_2H_5$. These facts point to the relations expressed in the formulas, $R-S-CN$ for the sulpho-cyanates, and $R-N-CS$ for the iso-sulpho-cyanates or mustard-oils.

---

In reviewing now the compounds of the hydrocarbons which are related to cyanogen, we see that there are two isomeric series of these, the names and general formulas of which are given below: —

| | | |
|---|---|---|
| Cyanides, $R-C-N$ . . . | Isocyanides or Carbamines, | $R-N-C$. |
| Cyanates, $R-O-CN$ . . . | Isocyanates, | $R-N-CO$. |
| Sulpho-cyanates, $R-S-CN$ . | Iso-sulpho-cyanates or Mustard oils, | $R-N-CS$. |

NOTE FOR STUDENT. — Study these compounds until the exact connection between the formulas and the facts above stated is clearly seen.

### SUBSTITUTED AMMONIAS.

When brom-ethane or any similar substitution-product is treated with ammonia, the reactions represented by the following equations take place step by step: —

$$
\begin{aligned}
C_2H_5Br + NH_3 &= NH_2(C_2H_5).HBr;\\
C_2H_5Br + NH_2(C_2H_5) &= NH(C_2H_5)_2.HBr;\\
C_2H_5Br + NH(C_2H_5)_2 &= N(C_2H_5)_3.HBr;\\
C_2H_5Br + N(C_2H_5)_3 &= N(C_2H_5)_4Br.
\end{aligned}
$$

The first three products are salts of hydrobromic acid, and bodies which in all their properties very closely resemble ammonia. When these salts are distilled with potassium hydroxide they are decomposed, just as ammonium bromide would be. Only instead of getting ammonia and potassium bromide, we get the compounds *ethyl-amine*, $NH_2.C_2H_5$, *di-ethyl-amine*, $NH(C_2H_5)_2$, and *tri-ethyl-amine*, $N(C_2H_5)_3$. These substances may be regarded as derived from ammonia by the replacement of one, two, and three of the hydrogen atoms respectively by ethyl. The last product of the series of reactions represented above may be regarded as ammonium bromide, $NH_4Br$, in which all four hydrogen atoms are replaced by ethyl groups.

The decomposition by potassium hydroxide of the first two salts is represented thus: —

$$
\begin{aligned}
NH_2(C_2H_5).HBr + KOH &= NH_2(C_2H_5) + KBr + H_2O;\\
NH(C_2H_5)_2.HBr + KOH &= NH(C_2H_5)_2 + KBr + H_2O.
\end{aligned}
$$

**Methyl-amine, $NH_2.CH_3$.** — This compound may be prepared by treating iodo-methane with ammonia: —

$$CH_3I + NH_3 = NH_2CH_3.HI.$$

It was first made by treating methyl isocyanate, $CH_3-N-CO$, with caustic potash: —

$$CH_3-N-CO + H_2O = NH_2.CH_3 + CO_2.$$

It has been stated that it is formed by treating hydrocyanic acid with nascent hydrogen: —

$$HCN + 4\,H = NH_2.CH_3.$$

It occurs in nature in herring brine, and is one of the products of the distillation of animal matter as well as of wood. It is now prepared on the large scale from certain waste products obtained in the refining of beet sugar (see Tri-methyl-amine).

Methyl-amine is a gas not easily condensed to a liquid. It smells like ammonia. It is, like ammonia, extremely easily soluble in water, 1 volume of water at 12.5° taking up 1150 volumes of the gas. This solution acts almost exactly like a solution of ammonia in water. It is strongly alkaline. It precipitates the metallic hydroxides, but, unlike ammonia, it does not redissolve precipitated hydroxides of nickel, cobalt, and cadmium when added in excess. Like ammonia, it dissolves aluminium hydroxide.

Methyl-amine forms salts with acids in the same way that ammonia does; that is, by direct addition. The action towards nitric and sulphuric acids takes place in accordance with the following equations: —

$$NH_2CH_3 + HNO_3 = NH_3CH_3.NO_3;$$
$$2\,NH_2CH_3 + H_2SO_4 = (NH_3CH_3)_2SO_4.$$

These salts are called methyl-ammonium nitrate and methyl-ammonium sulphate respectively.

**Di-methyl-amine, $NH(CH_3)_2$.** — This is formed by heating iodo-methane with alcoholic ammonia: —

$$2\,CH_3I + 2\,NH_3 = NH(CH_3)_2.HI + NH_4I.$$

It is formed, together with methyl-amine, as a product of the distillation of wood.

It is a gas which condenses to a liquid at + 8°. Its properties are much like those of methyl-amine.

**Tri-methyl-amine, $N(CH_3)_3$.** — Tri-methyl-amine is formed as one of the products of the treatment of iodo-methane with ammonia. It occurs widely distributed in nature, as in the blossoms of the hawthorn, the wild cherry, and the pear. It is contained in herring brine, and is a common product of the decomposition of organic substances which contain nitrogen. It is now obtained in large quantities from the so-called "vinasses." These are the waste liquids obtained in the refining of beet sugar. When the "vinasses" are evaporated to dryness, tri-methyl-amine is given off among the volatile products. It is collected as the hydrochloric acid salt, $N(CH_3)_3 . HCl$, which, when heated to 260°, yields ammonia, tri-methyl-amine, and chlor-methane: —

$$3\,N(CH_3)_3 . HCl = 2\,N(CH_3)_3 + NH_3 + 3\,CH_3Cl.$$

The chlor-methane is utilized for the purpose of producing low temperatures.

Tri-methyl-amine is a liquid boiling at 9° to 10°. It has a strong ammoniacal and fishy odor. It is very soluble in water and alcohol, and is a strong base. It is used in the preparation of potassium carbonate, by the Solvay process. In making sodium carbonate from the chloride by this method, acid ammonium carbonate is brought together with the chloride. Thus mono-sodium carbonate is precipitated, and ammonium chloride is left in solution. But mono-potassium carbonate and ammonium chloride are about equally soluble, so that potassium carbonate cannot be prepared in the same way. On the other hand, if tri-methyl-amine be substituted for ammonia, the separation can be effected, inasmuch as tri-methyl-ammonium chloride is more soluble than ammonium chloride.

NOTE FOR STUDENT. — Write the equations representing the reactions involved in making potassium carbonate from potassium chloride by means of tri-methyl-amine.

The ethyl-amines are very much like the methyl compounds, and hence need not be specially described.

When tri-ethyl-amine is brought together with iodo-ethane, the two unite, forming the compound tetra-ethyl-ammonium iodide, $N(C_2H_5)_4I$, which is ammonium iodide, in which all four hydrogen atoms have been replaced by ethyl groups. If silver oxide be added to the aqueous solution of the iodide, silver iodide is precipitated, and by evaporation of the liquid, crystals of *tetra-ethyl-ammonium hydroxide*, $N(C_2H_5)_4OH$, are obtained. This is plainly the hypothetical ammonium hydroxide, in which the four ammonium hydrogens have been replaced by ethyl. *Its solution acts almost like caustic potash.* It is very caustic, attracts carbon dioxide from the air, saponifies (see p. 70) ethereal salts, and gives the same precipitates as caustic potash. The reactions of the substituted ammonias above described make it certain that these bodies are very closely related to ammonia. The methods of formation also point clearly to the same conclusion. This relation is best expressed by the formulas above given.

Another method for the formation of substituted ammonias in which but one radical is present, as ethyl-amine, $NH_2.C_2H_5$, or in general $NH_2.R$, consists in treating with nascent hydrogen compounds known as *nitro compounds*, which are substitution-products containing the group $(NO_2)$ in the place of hydrogen. Thus, for example, when nitro-methane, $CH_3.NO_2$ (which see), is treated with hydrogen, the reaction which takes place is represented thus: —

$$CH_3.NO_2 + 6\,H = CH_3.NH_2 + 2\,H_2O.$$

In connection with another series, it will be shown that this reaction is a most important one, from the practical as well as the scientific stand-point. It may be said in anticipation that the manufacture of aniline, and consequently of all the many valuable dye-stuffs related to aniline, is based upon this reaction.

Just as we may look upon methyl-amine and the related bodies, as ammonia, in which one hydrogen atom is replaced by methyl, so also we may regard them, and with equal right, as marsh gas, in which hydrogen has been replaced by the group or residue $NH_2$. Owing to the frequency of the occurrence of this group in carbon compounds, and for the sake of simplifying the nomenclature, the group has been called the *amide* or *amido* group, and the bodies containing it *amido-compounds*. Thus the compounds $NH_2 . C_2H_5$ may be called either *ethyl-amine* or *amido-ethane*, etc.

Similarly, those bodies which contain two hydrocarbon residues, as di-ethyl-amine, $NH(C_2H_5)_2$, are called *imido-compounds*, and the group NH the *imide* or *imido* group. Substituted ammonias containing one hydrocarbon residue are called *primary ammonia bases*. Those containing two residues, as di-ethyl-amine, $NH(C_2H_5)_2$, are known as *secondary ammonia bases*, and those containing three residues, as tri-ethyl-amine, $N(CH_3)_3$, are called *tertiary ammonia bases*.

Among the most important of the reactions of amido-compounds or primary bases is that which takes place when they are treated with nitrous acid. Take ethyl-amine as an illustration. In order to understand what takes place when this compound is treated with nitrous acid, it is necessary to keep in mind the fact that the compound itself is a modified ammonia, and hence we may expect that its reactions will be but modifications of those which take place with ammonia. Thus with nitrous acid ammonia unites directly to form ammonium nitrite: —

$$NH_3 + HNO_2 = NH_4 . NO_2.$$

So also ethyl-amine forms ethyl-ammonium nitrite: —

$$NH_2 . C_2H_5 + HNO_2 = NH_3(C_2H_5) . NO_2.$$

Now we know that ammonium nitrite breaks up readily into free nitrogen and water: —

$$NH_4.NO_2 = N_2 + H_2O + H_2O.$$

So also ethyl-ammonium nitrite breaks up into free nitrogen, water, and *alcohol*: —

$$NH_3(C_2H_5)NO_2 = N_2 + H_2O + C_2H_5.OH.$$

The two reactions are strictly analogous. As in the second case we start with a substituted ammonia, we get as a product a *substituted water* or alcohol.

This reaction has been used very extensively in the preparation of bodies containing hydroxyl. For ordinary alcohol, as is clear, it is not a convenient method of preparation; but it will be shown that there are hydroxides for the preparation of which it is by far the most convenient method. The essential character of the transformation effected by it will be best understood by comparing the formulas of the amide and the alcohol. We have ethyl-amine, $C_2H_5.NH_2$, and from it we get alcohol, $C_2H_5.OH$. Thus we see that the transformation consists in replacing the amido-group by hydroxyl.

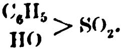
### HYDRAZINE COMPOUNDS.

Of late a class of bodies has been studied, the members of which bear the same relation to the hypothetical body, $N_2H_4$ (or $H_2N - NH_2$), that the substituted ammonias bear to ammonia. The reactions by which they are prepared are somewhat complicated, and they do not play an important part in the study of carbon compounds. A mere mention of their existence will therefore suffice for our present purpose.

### NITRO-COMPOUNDS.

Reference has already been made to a class of bodies containing the group $NO_2$, and known as nitro-compounds. They are most readily made by treating the hydrocarbons with nitric acid. This method, however, is not applicable to the hydrocarbons methane and ethane and their homologues, as these may be treated with nitric acid without undergoing change. The hydrocarbon benzene, $C_6H_6$, is acted upon very easily by nitric acid, when the reaction represented by the following equation takes place: —

$$C_6H_6 + HO.NO_2 = C_6H_5.NO_2 + H_2O.$$

The action is like that which takes place between sulphuric acid and benzene, which gives the sulphonic acid $C_6H_5.SO_2OH$ or  $\genfrac{}{}{0pt}{}{C_6H_5}{HO}{>}SO_2$. (See p. 76.) In each case a hydroxyl of the acid is replaced by the simple residue of the hydrocarbon. The product in the case of the bibasic acid, sulphuric acid, is itself still acid, while the product in the case of the monobasic nitric acid, is not an acid.

The nitro-derivatives of methane have been made by a reaction which we would expect to yield ethereal salts of nitrous acid; namely, by treating iodo-methane or ethane with silver nitrite: —

$$CH_3I + AgNO_2 = CH_3NO_2 + AgI.$$

The compound $CH_3.NO_2$, which is known as *nitro-methane*, does not conduct itself like the ethereal salts of nitrous acid. The latter are unstable bodies, while the former is stable.

Note for Student. — Compare the reaction just referred to with that which takes place between silver cyanide and iodo-methane; and that which takes place between iodo-ethane and potassium sulphite. What analogy is there to the former and to the latter?

It has already been stated that the nitro-derivatives are converted by nascent hydrogen into the corresponding amido-derivatives (see p. 97).

Note for Student. — Write the equations representing the reactions necessary to convert methyl alcohol into methyl-amine by means *of the nitro-compound.*

**Nitroform, $CH(NO_2)_3$,** as the formula indicates, is the tri-nitro-derivative of methane, or tri-nitro-methane. It is converted into *tetra-nitro-methane*, $C(NO_2)_4$, when treated with a mixture of concentrated sulphuric and fuming nitric acids.

**Nitro-chloroform, $C(NO_2)Cl_3$,** called also *chlorpicrin* and *nitro-trichlormethane*, is formed by distilling methyl or ethyl alcohol with common salt, saltpetre, and sulphuric acid. It is formed from a number of more complicated nitro-compounds, by distilling them with bleaching lime or hydrochloric acid and potassium chlorate.

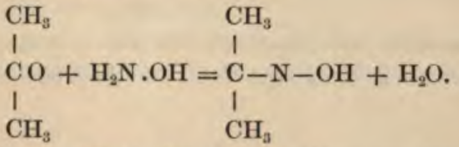
### NITROSO- AND ISONITROSO-COMPOUNDS.

When a compound containing the group CH is treated with nitrous acid, a reaction takes place, which is represented thus: —

$$R.CH + HO.NO = R.C.NO + H_2O.$$

The product R.C.NO, which is derived from the original substance by the substitution of the group NO for a hydrogen atom, is called a *nitroso-compound*. By oxidation the nitroso-compounds are converted into nitro-compounds, and by reduction they yield the same products as the corresponding nitro-compounds.

The isonitroso-compounds are isomeric with the nitroso-compounds. They are formed whenever acetones or aldehydes are treated with hydroxylamine, $NH_2.OH$. Assuming that the latter substance is really a hydroxyl derivative of ammonia, the reaction may be represented thus: —



$$\begin{array}{l}CH_3\\ \vert\\ CO\\ \vert\\ CH_3\end{array} + H_2N.OH = \begin{array}{l}CH_3\\ \vert\\ C-N-OH\\ \vert\\ CH_3\end{array} + H_2O.$$

The hydrogen of the hydroxyl has acid properties. The isonitroso-compounds are readily broken up, yielding, as one of *the products*, hydroxylamine.

**Fulminic acid,** $C_2N_2O_2H_2$, according to recent investigations, appears to be an isonitroso-compound, and for that reason finds appropriate mention in this place. The principal compound of fulminic acid, is the mercury salt, $C_2N_2O_2Hg$, commonly known as *fulminating mercury*. It is prepared by dissolving mercury in strong nitric acid, and adding alcohol to the solution. It is extremely explosive. Mixed with potassium nitrate it is used for filling percussion-caps.

When fulminating mercury is treated with concentrated hydrochloric acid, it yields hydroxylamine as one of the products of decomposition. This is regarded as evidence that fulminic acid is an isonitroso-compound. As will be seen, fulminic acid is isomeric with cyanic and cyanuric acids (see pp. 83 and 84).

## CHAPTER VII.

# DERIVATIVES OF METHANE AND ETHANE CONTAINING PHOSPHORUS, ARSENIC, ETC.

**Phosphorus compounds.**—Corresponding to the amines or substituted ammonias are the phosphines, which, as the name implies, are related to phosphine, $PH_3$. Methyl-phosphine, $PH_2.CH_3$, di-methyl-phosphine, $PH(CH_3)_2$, and tri-methyl-phosphine, $P(CH_3)_3$, may be taken as examples.

These substances, like the corresponding amines, form salts with acids, though not as readily. The hydroxide, *tetra-ethyl-phosphonium hydroxide*, $P(C_2H_5)_4.OH$, is a very strong base, though not as strong as the corresponding nitrogen derivative.

The phosphines have one marked property which distinguishes them from the amines, and that is their power to take up oxygen and form acids. Thus, ethyl-phosphine, $PH_2.C_2H_5$, when treated with nitric acid, is converted into *ethyl-phosphinic acid*, $PO(C_2H_5)(OH)_2$, a bibasic acid, bearing to phosphoric acid the same relation that the *sulphonic* acids bear to sulphuric acid.

Note for Student.—What is the relation? What other class of acids bears the same relation to carbonic acid?

Di-ethyl-phosphine, $PH(C_2H_5)_2$, yields *di-ethyl-phosphinic acid*, $PO(C_2H_5)_2.OH$, when oxidized.

These compounds are not commonly met with, and do not play a very important part in the study of the compounds of carbon.

**Arsenic compounds.**—The most characteristic carbon compound containing arsenic is that which is known as *cacodyl*, a name given to it on account of its extremely disagreeable odor (from κακώδης, *stinking*). It is prepared by distilling a mixture of potassium acetate and arsenic trioxide. The reactions which take place are very complicated, and many products are formed. Chief among the products is *cacodyl oxide:* —

$$4\,CH_3.CO_2K + As_2O_3 = [(CH_3)_2As]_2O + 2\,K_2CO_3 + 2\,CO_2.$$

When treated with hydrochloric acid, the oxide is converted into the *chloride* $(CH_3)_2AsCl$; and, when the chloride is treated with zinc, cacodyl itself is produced. Its analysis and the determination of its molecular weight lead to the formula $As_2C_4H_{12}$, which in all probability should be represented thus: $\left.\begin{matrix}(CH_3)_2As\\(CH_3)_2As\end{matrix}\right\}$. Cacodyl appears thus as a compound analogous to the hydrazines referred to above. (See p. 99.)

NOTE FOR STUDENT. — In what does the analogy consist?

Many derivatives of cacodyl have been made, but their study would hardly be profitable to the beginner.

By treating the chlorides of silicon, boron, and many of the metals with zinc ethyl, $Zn(C_2H_5)_2$, many similar ethyl derivatives have been made.

**Zinc ethyl** itself is made by treating iodo-ethane, $C_2H_5I$, with zinc alone or with zinc sodium: —

$$ZnNa_2 + 2\,C_2H_5I = Zn(C_2H_5)_2 + 2\,NaI.$$

It is a liquid boiling at 118°. It takes fire in the air, and burns with a white flame.

**Sodium-ethyl, $C_2H_5Na$,** may be obtained in combination with zinc ethyl by treating the latter with sodium. Both these compounds have been used to a considerable extent in the synthesis of carbon compounds, particularly the more complex hydrocarbons, and they will be frequently referred to in the following pages.

NOTE FOR STUDENT.—What is formed when sodium methyl and carbon dioxide are allowed to act upon each other?

Many of the derivatives, like the above, are volatile liquids. Such, for example, are mercury ethyl, $Hg(C_2H_5)_2$, aluminium ethyl, $Al(C_2H_5)_3$, tin tetrethyl, $Sn(C_2H_5)_4$, and silicon tetrethyl, $Si(C_2H_5)_4$. The study of these compounds has been of assistance in enabling chemists to determine the atomic weights of some of the elements which do not form simple volatile compounds.

## RETROSPECT.

In the introductory chapter (p. 19) these words were used in describing the plan to be followed: "Of the first series of hydrocarbons *two* members will be considered. Then the derivatives of these two will be taken up. These derivatives will serve admirably as representatives of the corresponding derivatives of other hydrocarbons of the same series and of other series. Their characteristics and their relations to the hydrocarbons will be dwelt upon, as well as their relations to each other. Thus, by a comparatively close study of two hydrocarbons and their derivatives, we may acquire a knowledge of the principal classes of the compounds of carbon. After these typical derivatives have been considered, the entire series of hydrocarbons will be taken up *briefly*, only such facts being dealt with at all fully as are not illustrated by the first two members."

In accordance with the plan thus sketched we have thus far considered the principal derivatives of the two hydrocarbons, methane and ethane, so far as these derivatives represent distinct classes of compounds. These derivatives were classified first into (1) those containing halogens; (2) those containing oxygen; (3) those containing sulphur; and (4) those containing nitrogen. On examining each of these classes more closely, we found that the halogen derivatives, such as chlor-methane, brom-ethane, etc., bear very simple relations to each other.

We found that under the head of oxygen derivatives, the most important and most distinctly characteristic derivatives of hydro-carbons are met with; as, the *alcohols*, *ethers*, *aldehydes*, *acids*, *ethereal salts*, and *ketones*. The sulphur derivatives, some of which closely resemble the oxygen derivatives, include the *sulphur alcohols* or *mercaptans*, *sulphur ethers*, and *sulphonic acids*.

On beginning the consideration of the nitrogen derivatives we found it desirable first to take up certain derivatives containing the cyanogen group, among which are cyanogen, hydrocyanic acid, cyanic acid, and sulphocyanic acid. Many interesting carbon compounds are closely related to these fundamental compounds. Such, for example, are the *cyanides* and *carbamines*, the *cyanates* and *isocyanates*, the *sulpho-cyanates* and *iso-sulpho-cyanates* or *mustard-oils*. Following the compounds related to cyanogen, we took up the interesting compounds which are related to ammonia, the *substituted ammonias* or *amines*. Then came the *nitro-derivatives;* and, finally, the compounds of the hydrocarbon residues or radicals with metals.

It is of the greatest importance that the student should master the preceding portion of this book. If he studies carefully the reactions which have been considered, and which are statements in chemical language which tell us the conduct of the various classes of derivatives, and if he performs the experiments which have been described, he will have a fair general knowledge of the kinds of relations which are met with in connection with the compounds of carbon through the whole field. As stated in the Introduction: "If we know what derivatives one hydrocarbon can yield, we know what derivatives we may expect to find in the case of every other hydrocarbon."

The more the student practises the use of the equations thus far given, the better he will be prepared to follow the remaining portions of the book. Indeed, it may be said that, if he thoroughly understands what has gone before, what follows will *appear extremely* simple. Whereas, if he has failed at any point to catch the exact meaning, if he has failed to see the connection, he had better go back and faithfully review, or he will soon find his mind hopelessly muddled, and relations which are as clear as day will be concealed from him.

A very excellent practice is to trace connections between the different classes of compounds, and show how to pass from one to the other. Thus, for example, (1) show by what reactions it is possible to pass from marsh gas to acetic acid. (2) How can we pass from ordinary alcohol to ethylidene chloride, $CH_3.CHCl_2$? (3) What reactions would enable us to make methyl-amine from its elements? (4) How may acetone be made from methyl-amine? (5) What reactions are necessary in order to make ordinary ether from ethyl-amine? etc., etc. It is well in this sort of practice to select what appear to be the least closely-related compounds, and to show then how we may pass from one to the other. Be sure to select representatives of all the classes hitherto mentioned, and to bring in all the important reactions.

# CHAPTER VIII.

## THE HYDROCARBONS OF THE MARSH-GAS SERIES, OR PARAFFINS.

THE existence of the homologous series of hydrocarbons beginning with methane and ethane was spoken of before its first two members were considered. A general idea of the extent of the series, and of the names used to designate the members, may be gained from the following table: —

**MARSH-GAS HYDROCARBONS.**

PARAFFINS. — HYDROCARBONS, $C_nH_{2n+2}$.

| | | Boiling-Point. |
|---|---|---|
| Methane | $CH_4$ | gas. |
| Ethane | $C_2H_6$ | gas. |
| Propane | $C_3H_8$ | gas. |
| Butane | $C_4H_{10}$ | 1°. |
| Pentane | $C_5H_{12}$ | 38°. |
| Hexane | $C_6H_{14}$ | 70°. |
| Heptane | $C_7H_{16}$ | 98.4°. |
| Octane | $C_8H_{18}$ | 125°. |
| Nonane | $C_9H_{20}$ | 148°. |
| Dodecane | $C_{12}H_{26}$ | 202°. |
| Hecdecane | $C_{16}H_{32}$ | 278°. |

The explanation of the remarkable relation in composition existing between these members, a relation to which the name *homology* is given, has already been referred to (p. 22). The number of hydrogen atoms contained in a member of this series bears a constant relation to the number of carbon atoms, as expressed in the general formula $C_nH_{2n+2}$. On examining the column headed "Boiling-Point" it will be seen that, as we pass upward in the series, the boiling-point becomes higher and higher. The first three members are gases at ordinary temperatures, while the highest boils at 278°. The elevation in the boiling-point is to some extent regular, as will be observed. The difference between butane, $C_4H_{10}$, and pentane, $C_5H_{12}$, is $38 - 1 = 37°$; that between pentane and the next member is $70 - 38 = 32°$; between hexane and heptane it is $98.4 - 70 = 28.4°$; between heptane and octane, $125 - 98.4 = 26.6°$; and, finally, between octane and nonane the difference is $148 - 125 = 23°$. Thus it will be seen that the elevation in boiling-point caused by the addition of $CH_2$ decreases as we pass upward in the series. Other relations have been pointed out, but it would be premature to discuss them here.

The chief natural source of the paraffins is petroleum; but although this substance, which occurs in such enormous quantities in nature, undoubtedly contains a number of the members of the paraffin series, it is an extremely difficult matter to isolate them from the mixture. Prolonged fractional distillation is not sufficient for the purpose. If, however, some of the purest products which can thus be obtained be treated with concentrated sulphuric acid, and afterwards with concentrated nitric acid, and then washed and redistilled, they may be obtained in pure condition.

**Petroleum.**—Petroleum occurs in enormous quantities in several places. Among the most important localities are Pennsylvania, the Crimea, the Caucasus, Persia, Burmah, China, etc. In some places it issues constantly from the earth. Usually it is necessary to bore for it. When one of the cavities in which it is contained is punctured, the oil is forced out of a pipe inserted into the opening in a jet, in consequence of the pressure exerted upon it by the gaseous constituents. As first obtained, it is usually a dark, yellowish-green liquid, with an unpleasant odor. It varies in appearance according to the place in which it is found. American petroleum contains the lowest members of the paraffin series; and when the oil is exposed to the air the gases are given off.

*Refining of petroleum.* To render petroleum fit for use in lamps, it is necessary that the volatile portions should be removed, as they form explosive mixtures with air, just as marsh gas does. It is also necessary to remove the higher boiling portions, because they are semi-solid, and would clog the wicks of the lamps. The crude oil is therefore subjected to distillation, and only those parts which have a certain specific gravity or boil between certain points are used for illuminating purposes, under the name of *kerosene*. Besides being distilled, the oil must further be treated with concentrated sulphuric acid, which removes a number of undesirable substances, and afterwards with an alkali, and then with water. All these processes taken together constitute what is called the refining of petroleum. In the distillation, the lighter products are usually divided into several parts, according to the specific gravity or boiling-point. Thus we have the products *cymogene*, *rhigolene*, *gasoline*, *naphtha*, and *benzine*, all of which are lighter than kerosene. It must be distinctly understood that none of the substances here mentioned are pure chemical substances. The names are commercial names, each of which applies to a complex mixture of hydrocarbons. From the heavier products, that is, those that boil at higher temperatures than the highest limit for kerosene, *paraffin*, which is a mixture of the highest members of this series, is made.

Owing to the danger attendant upon the use of improperly refined petroleum, laws have been enacted relating to the properties which the kerosene exposed for sale must have. These laws, which differ somewhat in different countries and different parts of the same country, relate mostly to what is called the *flashing-point*. This is the temperature to which the oil must be heated before it takes fire when a flame is applied to it. The legal flashing-point in many parts of the United States is 44°. Various forms of apparatus have been devised for the purpose of making the determination of the flashing-point as accurately as possible. Among them the following commends itself by its simplicity: The cylinder *A* is 2 to $3^{\text{cm}}$ in diameter and 10 to $12^{\text{cm}}$ long. Just within the wooden cork the bent tube contracts to a small orifice. At *d* it is connected by rubber-tubing with a source of compressed air (hand-bellows or gas holder), the flow of which can be controlled by the pinch-cock. *A* is about one-third filled with kerosene, and secured in a clamp, so that it plunges in a water-bath to the level of the oil. Air is now passed through *dcb*, and *e* so adjusted that about $0.5^{\text{cm}}$ foam is kept on the surface of the oil. From degree to degree the test is made by bringing a small flame for an instant to the mouth of *A*. At the flashing-point the vapor ignites, and the bluish flame runs down to the surface of the oil.

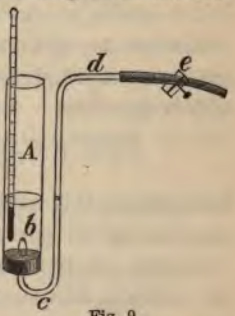


Fig. 9.

**Experiment 31.** Make an apparatus like the above, and determine the flashing-points of two or three specimens of kerosene which may be available.

**Synthesis of the paraffins.** — Although the paraffins do occur in nature, and some of them may be obtained in pure condition from natural sources, we are dependent upon synthetical operations performed in the laboratory for our knowledge of the series and the relations existing between them.

We have already seen how ethane may be prepared from methane by treating methyl iodide with zinc or sodium, as represented in this equation: —

$$CH_3I + CH_3I + 2\,Na = C_2H_6 + 2\,NaI.$$

This method has been extensively used in the building up of higher members of the series. Thus from ethane we may make ethyl iodide, and by treating this with sodium get butane $C_4H_{10}$: —

$$C_2H_5I + C_2H_5I + 2\,Na = C_4H_{10} + 2\,NaI.$$

But we may get the intermediate member, propane, $C_3H_8$, by mixing methyl iodide and ethyl iodide and treating the mixture with sodium: —

$$CH_3I + C_2H_5I + 2\,Na = CH_3.C_2H_5 + 2\,NaI.$$

By applying this method, it is plain that a large number of the members of the paraffin series might be made.

Another method consists in treating the zinc compounds of the radicals, like zinc ethyl, $Zn(C_2H_5)_2$, with the iodides of radicals. Thus zinc methyl and methyl iodide give ethane; zinc ethyl and ethyl iodide give butane; zinc ethyl and methyl iodide give propane, etc.: —

$$\begin{aligned} Zn(CH_3)_2 + 2\,CH_3I &= 2\,C_2H_6 + ZnI_2; \\ Zn(C_2H_5)_2 + 2\,C_2H_5I &= 2\,C_4H_{10} + ZnI_2; \\ Zn(C_2H_5)_2 + 2\,CH_3I &= 2\,C_3H_8 + ZnI_2. \end{aligned}$$

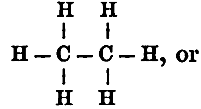
Paraffins may be made by replacing the halogen in a substitution-product by hydrogen. This may be effected by nascent hydrogen or by hydriodic acid: —

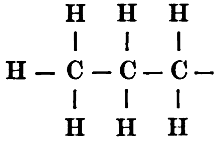
$$C_4H_9I + 2\,H = C_4H_{10} + HI.$$

Finally, the paraffins may be made by heating the acids of the formic acid series with an alkali. This has been illustrated by the preparation of marsh gas from acetic acid by heating with lime and caustic potash. The reaction may be written thus: —

$$CH_3.CO_2K + KOH = CH_4 + CO_3K_2.$$

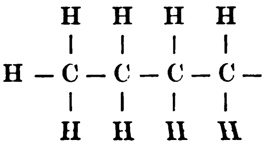
The *products* are a hydrocarbon and a carbonate.

**Isomerism among the paraffins.** — It has already been stated that the evidence is almost conclusive that each of the four hydrogen atoms of marsh gas bears the same relation to the carbon, and hence we believe that, as regards the nature of the product, it makes no difference which hydrogen atom is replaced by a given atom or radical. According to this, as ethane is the methyl derivative of marsh gas, it makes no difference which of the hydrogen atoms of marsh gas is replaced by the methyl, the product must always be the same, or *there is but one ethane possible according to the theory.* This is represented by the formula,  $\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$, or $H_3C-CH_3$. In ethane, as well as in methane, all the hydrogen atoms bear the same relation to the molecule, and it should make no difference which one is replaced by methyl. But propane is regarded as derived from ethane by the substitution of methyl for hydrogen; and, as it makes no difference which hydrogen is replaced, *there is but one propane possible.* Only one has ever been discovered, and this must be represented thus: —



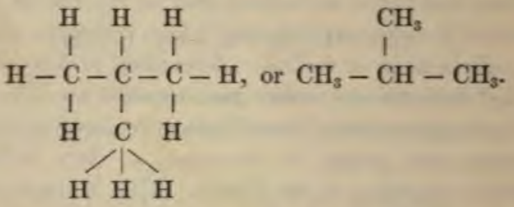
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}, \text{ or } CH_3.CH_2.CH_3.$$

Now, continuing the process of substitution of methyl for hydrogen, it appears that the theory indicates the possibility of the existence of two compounds of the formula $C_4H_{10}$. One of these should be obtained by replacing by methyl one of the three hydrogens of either methyl group of propane. It is represented by the formula: —



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}, \text{ or } H_3C.CH_2.CH_2.CH_3.$$

The other should be obtained by replacing by methyl one of the two hydrogens of the group $CH_2$ contained in propane. This would give a hydrocarbon of the formula:—

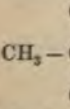


$$\mathrm{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_3}.$$

The theory then indicates the existence of two butanes. How about the facts? Two, and only two butanes have been discovered. The first, which occurs in American petroleum, has been made synthetically by treating ethyl iodide with zinc:—

$$2\,CH_3.CH_2I + Zn = CH_3.CH_2.CH_2.CH_3 + ZnI_2.$$

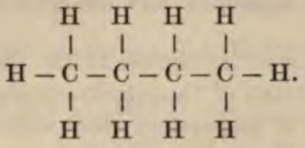
The method of synthesis clearly shows which of the two possible isomerides the product is. It is known as **normal butane.** It is a gas which can be condensed to a liquid at +1°.

The second, or **isobutane**, is made from an alcohol which will be shown to have the structure represented by the formula  $\mathrm{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - OH}$ (see Tertiary Butyl Alcohol, p. 124), by replacing the hydroxyl by hydrogen. It is a gas which becomes liquid at $-17°$.

The differences between the two butanes are observed principally in their derivatives.

Applying the same method of consideration to the next member of the series, how many isomeric varieties of pentane, $C_5H_{12}$, may we expect to find? The question resolves itself into a determination of the number of kinds of hydrogen atoms contained in the two butanes, or the number of relations to the *molecule represented* among the hydrogen atoms of the butanes.

We can make this determination best by examining the structural formulas. Take first normal butane: —



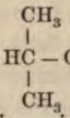
$$\begin{array}{ccccccccc} & & H & & H & & H & & H \\ & & | & & | & & | & & | \\ H & - & C & - & C & - & C & - & C - H. \\ & & | & & | & & | & & | \\ & & H & & H & & H & & H \end{array}$$

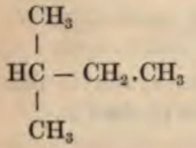
In this there are plainly two different relations represented; viz., that of each of the six hydrogens in the two methyl groups, and that of each of the four hydrogens of the two $CH_2$ groups. The two possible methyl derivatives of a hydrocarbon of this formula are therefore to be represented thus: —

$$H_3C.CH_2.CH_2.CH_2.CH_3, \qquad (1)$$

and

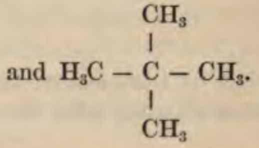
$$H_3C.CH_2.CH <\begin{matrix} CH_3 \\ CH_3 \end{matrix}. \qquad (2)$$

Now, taking isobutane,  $\begin{array}{l} CH_3 \\ | \\ HC - CH_3, \\ | \\ CH_3 \end{array}$ we see that it consists of three methyl groups, giving nine hydrogen atoms of the same kind, and one CH group, the hydrogen of which bears a different relation to the molecule from that which the other nine do. There are therefore two possible methyl derivatives of isobutane which must be represented thus: —



$$\begin{array}{l} CH_3 \\ | \\ HC - CH_2.CH_3 \\ | \\ CH_3 \end{array} \qquad (3),$$

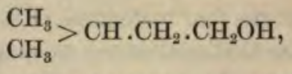
and



$$H_3C - \begin{array}{c} CH_3 \\ | \\ C \\ | \\ CH_3 \end{array} - CH_3. \qquad (4)$$

We have, therefore, apparently four pentanes. But on comparing formulas (2) and (3), it will be seen that, though written a little differently, they really represent one and the same compound. Thus the number of pentanes, the existence of which is indicated by the theory, is three, and these are represented by formulas (1), (2), and (4). *They are all known.* The first is called **normal pentane**, the second **iso-pentane** or **di-methyl-ethyl-methane**, and the third **tetra-methyl-methane.**

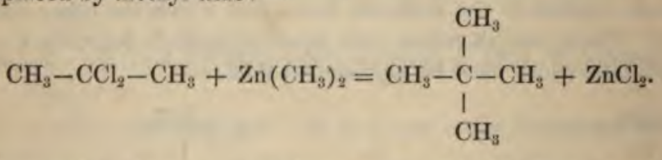
It would lead too far to discuss all the methods of preparation and the properties of these hydrocarbons. It will be seen that the methods of preparation show what the structure of a hydrocarbon is. Di-methyl-ethyl-methane is made from an alcohol which can be shown to have the formula



$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\mathrm{CH.CH_2.CH_2OH},$$

by replacing the hydroxyl by hydrogen. Hence its structure is that represented above by formulas (2) and (3).

Tetra-methyl-methane is made by starting with acetone. Acetone has been shown to consist of carbonyl in combination with two methyl groups, as represented in the formula $\mathrm{CH_3-CO-CH_3}$. It has also been shown that, by treating acetone with phosphorus pentachloride, the oxygen is replaced by chlorine, giving a compound of the formula $\mathrm{CH_3-CCl_2-CH_3}$. Now, by treating this chloride with zinc-methyl, the chlorine is replaced by methyl thus: —



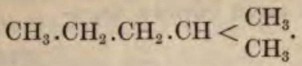
$$\mathrm{CH_3-CCl_2-CH_3 + Zn(CH_3)_2 = CH_3-}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\overset{|}{\underset{|}{\mathrm{C}}}}}\mathrm{-CH_3 + ZnCl_2}.$$

The product is tetra-methyl-methane, and the synthesis thus effected shows at once what the structure of the product is.

**Hexanes.** — The student will now be prepared to apply the theory to the determination of the number of hexanes possible. He will find that there are five. The theory is, in this case as in the preceding, in perfect accordance with the facts. There are five and only five hexanes known. Only the names and formulas of these will be given here: —

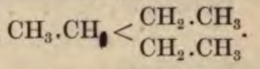
1. **Normal hexane,** $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$.

2. **Iso-hexane,**



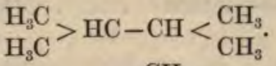
$$CH_3.CH_2.CH_2.CH<\begin{matrix}CH_3\\CH_3\end{matrix}.$$

3. **Methyl-di-ethyl-methane,**



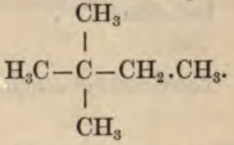
$$CH_3.CH<\begin{matrix}CH_2.CH_3\\CH_2.CH_3\end{matrix}.$$

4. **Tetra-methyl-ethane,**



$$\begin{matrix}H_3C\\H_3C\end{matrix}>HC-CH<\begin{matrix}CH_3\\CH_3\end{matrix}.$$

5. **Tri-methyl-ethyl-methane,**



$$\begin{matrix} & CH_3 & \\ & | & \\ H_3C- & C & -CH_2.CH_3. \\ & | & \\ & CH_3 & \end{matrix}$$

Passing upward, we find that *nine* heptanes are possible according to the theory, while but *four* have thus far been discovered; and that, while theory indicates the possibility of the discovery of *eighteen* hydrocarbons of the formula $C_8H_{18}$, but *three* are known. The theoretical number of isomeric varieties of the highest members of the series is very great, but our knowledge in regard to these highest members is very limited, and it is impossible to say whether the theory will ever be confirmed by facts. It may be that there is some law limiting the number of complicated hydrocarbons. It is, however, idle to speculate upon the subject at present. It is well for us to keep in mind that a thorough knowledge of a few of the simplest members of the series is all that is necessary for the present.

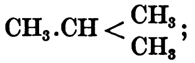
On examining the formulas used to express the structure of the hydrocarbons, we find that they may be divided into three classes: —

(1) Those in which there is no carbon atom in combination with more than two others; as, —

Propane . . . . $CH_3.CH_2.CH_3$;
Normal butane . . $CH_3.CH_2.CH_2.CH_3$;
Normal pentane . $CH_3.CH_2.CH_2.CH_2.CH_3$;
and Normal hexane . . $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$.

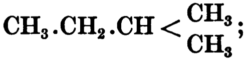
(2) Those in which there is at least one carbon atom in combination with three others; as,—

Isobutane . . . .



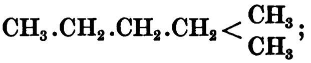
$CH_3.CH<\begin{matrix}CH_3\\CH_3\end{matrix};$

Isopentane . . .



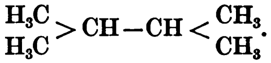
$CH_3.CH_2.CH<\begin{matrix}CH_3\\CH_3\end{matrix};$

Isohexane . . . .



$CH_3.CH_2.CH_2.CH_2<\begin{matrix}CH_3\\CH_3\end{matrix};$

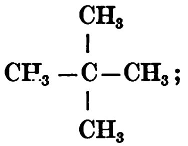
and Tetra-methyl-ethane,



$\begin{matrix}H_3C\\H_3C\end{matrix}>CH-CH<\begin{matrix}CH_3\\CH_3\end{matrix}.$

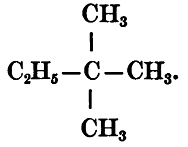
(3) Those in which there is at least one carbon atom in combination with four others; as,—

Tetra-methyl-methane . .



$$\begin{matrix} & CH_3 & \\ & | & \\ CH_3- & C & -CH_3; \\ & | & \\ & CH_3 & \end{matrix}$$

and Tri-methyl-ethyl-methane,



$$\begin{matrix} & CH_3 & \\ & | & \\ C_2H_5- & C & -CH_3. \\ & | & \\ & CH_3 & \end{matrix}$$

The members of the first class are called *normal paraffins;* those of the second class, *iso-paraffins;* and those of the third class, *neo-paraffins.*

Only the members of the same class are strictly comparable with each other. Thus it has been found that the boiling-points of the normal hydrocarbons bear simple relations to each other, and that the same is true of the iso-paraffins; but, on comparing the boiling-points and other physical properties of normal paraffins with those of the iso- or neo-paraffins, no such simple relations are observed.

Regarding the names of the paraffins, the simplest nomenclature in use is that according to which the hydrocarbons are all regarded as derivatives of methane. Thus we get the name ethyl-methane for propane, $C\left\{\begin{array}{l}C_2H_5\\H\\H\\H\end{array}\right.$; tri-methyl-methane for isobutane, $C\left\{\begin{array}{l}CH_3\\CH_3\\CH_3\\H\end{array}\right.$; tetra-methyl-methane, $C\left\{\begin{array}{l}CH_3\\CH_3\\CH_3\\CH_3\end{array}\right.$, etc.

# CHAPTER IX.

# OXYGEN DERIVATIVES OF THE HIGHER MEMBERS OF THE PARAFFIN SERIES.

We are now to take up the derivatives of the higher members of the paraffin series, just as we took up the derivatives of methane and ethane. Not much need be said in regard to the halogen derivatives. A few of them will be mentioned in connection with the corresponding alcohols. The chief substances which will require attention are the alcohols and acids.

## 1. Alcohols.

**Normal propyl alcohol, $C_3H_7.OH$.** — When sugar undergoes fermentation, a little propyl alcohol is always formed, and is contained in the "fusel oil." From this it may be separated by treating those portions which boil between 85° and 110° with phosphorus and bromine. The bromides of the alcohols present are thus formed (what is the reaction?), and these are separated by fractional distillation. The bromide corresponding to propyl alcohol is then converted into the alcohol (how may this be done?).

It is a colorless liquid with a pleasant odor. It boils at 97.4° (compare with the boiling-points of methyl and ethyl alcohol). It conducts itself almost exactly like the two first members of the series. By oxidation it is converted into an aldehyde, $C_3H_6O$, and an acid, $C_3H_6O_2$, which bear to it the same relations that acetic aldehyde and acetic acid bear to ethyl alcohol.

**Secondary propyl or isopropyl alcohol, $C_3H_7.OH$.** — The reasons for regarding the alcohols as hydroxyl derivatives of the hydrocarbons have been given pretty fully. As the six hydrogen atoms of ethane are all of the same kind, but one ethyl alcohol appears to be possible and only one is known. But just as there are two butanes or methyl derivatives of propane, so there are two hydroxyl derivatives of propane; or, in other words, two propyl alcohols. The first is the one obtained from "fusel oil," the other is the one called secondary propyl alcohol. This has already been referred to under the head of Acetone (see p. 72), where it was stated that acetone is converted into secondary propyl alcohol by nascent hydrogen. We are, in fact, dependent upon this method for the preparation of the alcohol.

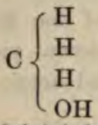
It is, like ordinary propyl alcohol, a colorless liquid. It boils at 85°. While all its reactions show that it is a hydroxide, under the influence of oxidizing agents it conducts itself quite differently from the alcohols thus far considered. It is converted first into acetone, $C_3H_6O$, which is isomeric with the aldehyde obtained from ordinary propyl alcohol; by further oxidation, it however does not yield an acid of the formula $C_3H_6O_2$, as we would expect it to, but breaks down, yielding two simpler acids; viz., formic acid, $CH_2O_2$, and acetic acid, $C_2H_4O_2$.

**Secondary alcohols.** — Secondary propyl alcohol is the simplest representative of a class of alcohols which are known as *secondary alcohols*. They are made by treating the ketones with nascent hydrogen, and are easily distinguished from other alcohols by their conduct towards oxidizing agents. They yield acetones containing the same number of carbon atoms, and then break down, yielding acids containing a smaller number of carbon atoms.

Is there anything in the structure of these secondary alcohols to suggest an explanation of their conduct? Secondary propyl alcohol is made from acetone by treating with nascent hydrogen. Acetone contains two methyl groups and carbonyl, as represented by the formula $CH_3-CO-CH_3$. The simplest change that we can imagine as taking place in this compound under the influence of hydrogen is that represented in the following equation:—

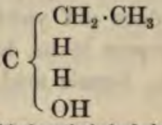
$$CH_3-CO-CH_3 + H_2 = CH_3-CH.OH-CH_3.$$

The very close connection existing between acetone and secondary propyl alcohol, and the fact that there are two methyl groups in acetone, make it appear probable that there are also two methyl groups in secondary propyl alcohol, as represented in the above equation. On the other hand, the easy transformation of primary propyl alcohol into propionic acid, which can be shown to contain ethyl, shows that in the alcohol ethyl is present. Therefore, we may conclude that the difference between primary and secondary propyl alcohol is that the former is an ethyl derivative and the latter a di-methyl derivative of methyl alcohol, as represented by the formulas:—



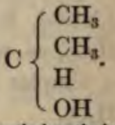
$$C\left\{\begin{array}{l}H\\H\\H\\OH\end{array}\right.$$

Methyl alcohol.



$$C\left\{\begin{array}{l}CH_2\cdot CH_3\\H\\H\\OH\end{array}\right.$$

Ethyl methyl alcohol or ordinary propyl alcohol.



$$C\left\{\begin{array}{l}CH_3\\CH_3\\H\\OH\end{array}\right.$$

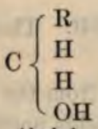
Dimethyl methyl alcohol or secondary propyl alcohol.

Primary propyl alcohol is *methyl alcohol in which one hydrogen is replaced by a radical*, while secondary propyl alcohol is *methyl alcohol in which two hydrogens are replaced by radicals*. An examination of all secondary alcohols known shows that the above statement may be made in regard to all of them. They must be regarded as derived from methyl alcohol by the replacement of two hydrogen atoms by radicals. The alcohols of the first class, like methyl, ethyl, and ordinary propyl alcohols, which are derived from methyl alcohol by the replacement of one hydrogen by a radical, are called *primary alcohols*. Another way of stating the difference between primary and secondary alcohols is this: Primary alcohols contain the group $CH_2OH$; secondary alcohols contain the group CHOH. These statements, as will be seen, are corollaries of the first ones.

A primary alcohol, when oxidized, yields an aldehyde and an acid containing the same number of carbon atoms as the alcohol does.

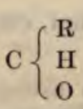
A secondary alcohol, when oxidized, yields an acetone, and then an acid or acids containing a smaller number of carbon atoms.

Recalling what was said regarding the nature of the changes involved in passing from an alcohol to the corresponding aldehyde and acid, we see that the formation of the acid is impossible in the case of a secondary alcohol. In the case of a primary alcohol, we have:—



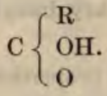
$C\begin{cases}R\\H\\H\\OH\end{cases}$

Alcohol.



$C\begin{cases}R\\H\\O\end{cases}$

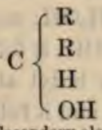
Aldehyde.



$C\begin{cases}R\\OH.\\O\end{cases}$

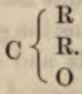
Acid.

In the case of the secondary alcohol, we have:—



$C\begin{cases}R\\R\\H\\OH\end{cases}$

Secondary alcohol.



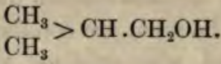
$C\begin{cases}R\\R.\\O\end{cases}$

Ketone.

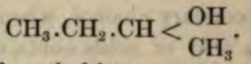
Further introduction of oxygen cannot take place without a breaking down of the compound. It will be seen that the formulas used to express the structure of the compounds are remarkably in accordance with the facts.

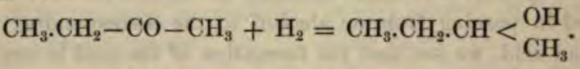
**Butyl alcohols, $C_4H_9.OH$.**—Theoretically, there are two possible hydroxyl derivatives of each of the two butanes, making four butyl alcohols in all. They are all known. Two are primary alcohols.

1. **Normal butyl alcohol,** $CH_3.CH_2.CH_2.CH_2.OH$.

2. **Isobutyl alcohol,**  $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2OH$.

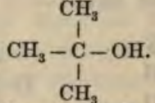
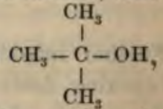
The third is a derivative of normal butane, and is a secondary alcohol.

3. **Secondary butyl alcohol,**  $CH_3.CH_2.CH<\begin{matrix}OH\\CH_3\end{matrix}$. This alcohol is prepared by treating ethyl-methyl ketone with nascent hydrogen: —



$$CH_3.CH_2-CO-CH_3 + H_2 = CH_3.CH_2.CH<\begin{matrix}OH\\CH_3\end{matrix}.$$

(Compare this with the reaction for making secondary propyl alcohol.)

4. **Tertiary butyl alcohol,**  $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$. The fourth butyl alcohol has properties which distinguish it from the primary and secondary alcohols. When oxidized it yields neither an aldehyde nor an acetone, but breaks down at once, yielding acids containing a smaller number of carbon atoms. Assuming that every primary alcohol contains the group $CH_2OH$, and that every secondary alcohol contains the group $CHOH$, it follows that the two primary butyl alcohols and secondary butyl alcohol must have the formulas above assigned to them; and it follows further, that the fourth butyl alcohol must have the formula  $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$, as this represents the only other arrangement of the constituents possible, according to our theory. This formula represents a condition which does not exist in either the primary or secondary alcohols. It is methyl alcohol in which all the hydrogen atoms, except that in the hydroxyl, are replaced by methyl groups, and it contains the group $C-(OH)$. Such an alcohol is known as a *tertiary alcohol*, and the one under consideration

is called *tertiary butyl alcohol*. It is the simplest derivative of a class of which but few members are known.

Tertiary butyl alcohol is made by a complicated reaction which cannot easily be interpreted; viz., by treating acetyl chloride, $CH_3.COCl$, with zinc methyl, $Zn(CH_3)_2$. These two substances unite, forming a crystallized compound; and, when this is treated with water, it breaks up, yielding several products, among which is tertiary butyl alcohol. By taking other acid chlorides, and the zinc compounds of other radicals, other tertiary alcohols may be obtained.

*Characteristics of the three Classes of Alcohols.* To recapitulate briefly, we find, in studying the hydroxyl derivatives of the hydrocarbons, that they can be divided into three classes, according to their conduct towards oxidizing agents.

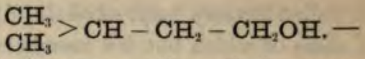
To what was said above regarding the conduct of primary and secondary alcohols we can now add: Tertiary alcohols yield neither aldehydes nor acetones, but break down at once, yielding simpler acids.

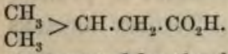
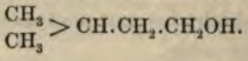
The general formulas representing these three kinds of alcohols are:—

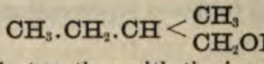
$$\underset{\text{Primary.}}{C\left\{\begin{matrix}R\\H\\H\\OH\end{matrix}\right.} \qquad \underset{\text{Secondary.}}{C\left\{\begin{matrix}R\\R\\H\\OH\end{matrix}\right.} \qquad \text{and} \qquad \underset{\text{Tertiary.}}{C\left\{\begin{matrix}R\\R\\R\\OH\end{matrix}\right.}$$

NOTE FOR STUDENT. — Show how the formula for the tertiary alcohols is in accordance with the fact that these alcohols do not yield aldehydes nor ketones.

**Pentyl alcohols, $C_5H_{11}.OH$.** — These alcohols are the hydroxyl derivatives of the pentanes. Eight are possible, and seven of these are known. Only two of them need be considered here. These are the so-called *amyl alcohols*.

**Inactive amyl alcohol,**  $\begin{matrix}CH_3\\CH_3\end{matrix}>CH-CH_2-CH_2OH$.—This alcohol, together with at least one other of the same composition, forms the chief part of the fusel oil obtained in the fermentation of sugar. By fractional distillation of fusel oil ordinary commercial amyl alcohol is obtained, as a colorless liquid, having a penetrating odor, and boiling at 131° to 132°. This can be separated by other methods into two isomeric alcohols, one of which is *inactive* amyl alcohol and the other *active* amyl alcohol. The names refer to the behavior of the substances towards polarized light, the former having no action upon it, the latter turning the plane of polarization[1] to the left.

When oxidized, inactive amyl alcohol yields an acid containing the same number of carbon atoms, and is, therefore, a primary alcohol. The acid has been made by simple reactions which show that it must be represented by the formula  $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2.CO_2H$. Therefore, the alcohol has the structure represented by the formula  $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2.CH_2OH$.

**Active amyl alcohol,**  $CH_3.CH_2.CH<\begin{matrix}CH_3\\CH_2OH\end{matrix}$.—This, as has been stated, is obtained, together with the inactive alcohol, from fusel oil. Not enough is known about it to enable us to say with certainty whether the above formula represents its structure or not. It is a primary alcohol as represented.

The remaining members of the series will not be considered, though a list of some of the more important ones is given below. As regards the naming of the alcohols, it is best to refer them to methyl alcohol, just as the hydrocarbons are referred to marsh gas. For this purpose methyl alcohol is called *carbinol*, and we then get such names as methyl-carbinol, di-ethyl-carbinol, etc., which convey at once an accurate idea concerning the structure of the substances. A few illustrations will suffice. Take the alcohols considered above: —

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[1] This is not the proper place to explain exactly what is meant by these expressions. To the student of physics they convey definite meanings. To one who has not studied physics they are meaningless.

Ethyl alcohol is *methyl-carbinol*, $C\left\{\begin{matrix}CH_3\\ H\\ H\\ OH\end{matrix}\right.$ ;

Primary propyl alcohol is *ethyl-carbinol*, $C\left\{\begin{matrix}CH_2CH_3\\ H\\ H\\ OH\end{matrix}\right.$ ;

Secondary propyl alcohol is *di-methyl-carbinol*, $C\left\{\begin{matrix}CH_3\\ CH_3\\ H\\ OH\end{matrix}\right.$ ;

Tertiary butyl alcohol is *tri-methyl-carbinol*, $C\left\{\begin{matrix}CH_3\\ CH_3\\ CH_3\\ OH\end{matrix}\right.$ ;

Inactive amyl alcohol is *isobutyl-carbinol*, $C\left\{\begin{matrix}CH_2.CH<\begin{matrix}CH_3\\ CH_3\end{matrix}\\ H\\ H\\ OH\end{matrix}\right.$ etc., etc.,

a name given to it on account of the presence in it of the isobutyl group $CH_2.CH<\begin{matrix}CH_3\\ CH_3\end{matrix}$.

The following table will give an imperfect idea of the extent to which the series of alcohols derived from the paraffins is developed. There are eight hexyl alcohols and four heptyl alcohols known. Of most of the higher members but one variety is known. They are not important, except in so far as they indicate the possibility of the discovery of other alcohols.

### ALCOHOLS OF THE METHYL ALCOHOL SERIES.

Series $C_nH_{2n+1}.OH$.

| | | |
|---|---|---|
| Methyl alcohol | | $CH_3.OH$. |
| Ethyl | " | $C_2H_5.OH$. |
| Propyl | " | $C_3H_7.OH$. |
| Butyl | " | $C_4H_9.OH$. |
| Pentyl | " | $C_5H_{11}.OH$. |
| Hexyl | " | $C_6H_{13}.OH$. |
| Heptyl | " | $C_7H_{15}.OH$. |
| Octyl | " | $C_8H_{17}.OH$. |
| Nonyl | " | $C_9H_{19}.OH$. |
| Cetyl | " | $C_{16}H_{33}.OH$. |
| Ceryl | " | $C_{27}H_{55}.OH$. |
| Myricyl | " | $C_{30}H_{61}.OH$. |

### 2. Aldehydes.

In general, it follows from what has been said concerning the properties of primary alcohols, that there should be an aldehyde corresponding to every primary alcohol. Many of these have been prepared. They resemble ordinary acetic aldehyde so closely that it is unnecessary to take them up individually. If we know the structure of the alcohol from which an aldehyde is formed by oxidation, we also know the structure of the aldehyde.

Besides the one method for the preparation of aldehydes which has been mentioned, viz., the oxidation of primary alcohols, there is one other which should be specially noticed. It consists in distilling a mixture of a formate and a salt of some other acid. Thus, if a mixture of an acetate and a formate be distilled, acetic aldehyde is formed as represented by the equation: —

$$\begin{matrix} CH_3.COOM \\ H.COOM \end{matrix} = \underset{\text{Aldehyde.}}{CH_3.COH} + M_2CO_3.$$

This method has been used to a considerable extent in making the higher members of the series.

**Experiment 32.** Mix about equal weights of dry potassium formate and dry sodium acetate. Distil from a small flask. Collect some of the distillate in water, and prove that aldehyde is formed.

### 3. Acids.

Formic and acetic acids are the first two members of an homologous series of similar acids, generally called the *fatty acids*, on account of the fact that several of them occur in large quantities in the natural fats. The names and formulas of some of the principal members are given in the following table. The reasons for representing the acids as compounds containing the carboxyl group, $CO_2H$, have been given, and need not here be restated: —

### FATTY ACIDS.

Series $C_nH_{2n+1}.CO_2H$, or $C_nH_{2n}O_2$.

| | | |
|---|---|---|
| Formic | acid | $H.CO_2H$. |
| Acetic | " | $CH_3.CO_2H$. |
| Propionic | " | $C_2H_5.CO_2H$. |
| Butyric | " | $C_3H_7.CO_2H$. |
| Valeric | " | $C_4H_9.CO_2H$. |
| Caproic or Hexoic acids | | $C_5H_{11}.CO_2H$. |
| Œnanthylic or Heptoic acids | | $C_6H_{13}.CO_2H$. |
| Caprylic or Octoic acids | | $C_7H_{15}.CO_2H$. |
| Pelargonic or Nonoic acids | | $C_8H_{17}.CO_2H$. |
| Capric | acid | $C_9H_{19}.CO_2H$. |

replacing the hydroxyl of this lactic acid by chlorine, α-chlor-propionic acid is formed. It therefore follows that formula (2) above given is that of α-chlor-propionic acid, and formula (1) that of β-chlor-propionic acid. Further, any mono-substitution product of propionic acid which can be made directly from α-chlor-propionic acid, or converted directly into this acid, is an α-product, and has the general formula

$$CH_3.CHX.CO_2H;$$

and, similarly, the β-products have the general formula

$$CH_2X.CH_2.CO_2H,$$

in which X represents any univalent atom or group.

**Butyric acids, $C_4H_8O_2(C_3H_7.CO_2H)$.**

*Normal butyric acid*, $CH_3.CH_2.CH_2.CO_2H$. When butter is boiled with caustic potash, the potassium salts of butyric acid and of some of the higher members of the series are found in the solution at the end of the operation. Butter, like other fats, belongs to the class of bodies known as ethereal salts; and these, as we have seen, when boiled with the alkalies are decomposed, yielding alcohol and alkali salts of acids (saponification). In the case of butter and of nearly all other fats, the alcohol formed is *glycerin*. Butyric acid occurs also in many other fats besides butter.

It is made most readily by fermentation of sugar by what is known as the *butyric acid ferment*. This ferment probably is contained in putrid cheese. Hence, to make the acid, sugar and tartaric acid are dissolved in water, and, after a time, certain quantities of putrid cheese and sour milk are added, and also some powdered chalk. At first the sugar is converted into glucose: —

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + H_2O = 2\,\underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

The glucose breaks up, yielding lactic acid, $C_3H_6O_3$: —

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = 2\,\underset{\text{Lactic acid.}}{C_3H_6O_3}.$$

And, finally, the lactic acid is converted into butyric acid: —

$$2\,C_3H_6O_3 = C_4H_8O_2 + 2\,CO_2 + 4\,H.$$

Other methods for the preparation of butyric acid are: —

(1) By oxidation of normal butyl alcohol; and

(2) By treating normal propyl cyanide, $CH_3.CH_2.CH_2CN$, with caustic potash.

The acid is a liquid having an acid, rancid odor, like that of rancid butter. It boils at 163°. (Compare with the preceding acids.) Like the lower members of the series it mixes with water in all proportions.

*Ethyl butyrate*, $C_3H_7.CO_2C_2H_5$, has a pleasant odor resembling that of pineapples. It is used under the name of *essence of pineapples*.

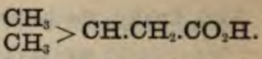
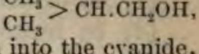
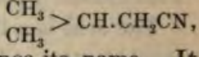
**Isobutyric acid, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}>CH.CO_2H$.** — From the two propyl alcohols the two chlorides, propyl chloride, $CH_3.CH_2.CH_2Cl$, and isopropyl chloride, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}>CHCl$, can be made, and from these the corresponding cyanides, —

| | | |
|---|---|---|
| | Propyl cyanide . . . . . | $CH_3.CH_2.CH_2CN$, |
| and | Isopropyl cyanide . . . . | $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}>CHCN$. |

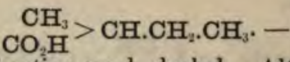
By boiling with caustic potash, the former is converted into normal butyric acid, as stated above; while the latter yields isobutyric acid, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}>CH.CO_2H$. This acid may be prepared also by oxidizing isobutyl alcohol, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}>CH.CH_2OH$. It is found in nature in the carob bean.

Isobutyric acid is a liquid which boils at 154°. Its odor is less unpleasant than that of the normal acid.

**Valeric acids, $C_5H_{10}O_2(C_4H_9.CO_2H)$.** — Four carboxyl derivatives of the butanes are possible. Four acids of the formula $C_5H_{10}O_2$ are known.

**Inactive or ordinary valeric acid,**  $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2.CO_2H$. — This acid is made by oxidizing inactive amyl alcohol. It may also be made (and this reaction reveals the structure of the acid) by starting with isobutyl alcohol,  $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2OH$, converting this first into the chloride and then into the cyanide, and, finally, transforming the cyanide, which is  $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2CN$, into the acid. It occurs in valerian root, whence its name. It is an unpleasant smelling liquid, boiling at 175°. It requires thirty parts of water for solution.

*Amyl valerate*, $C_4H_9.CO_2C_5H_{11}$, has the odor of apples, and is used under the name of *essence of apples*.

**Active valeric acid,**  $\begin{matrix}CH_3\\CO_2H\end{matrix}>CH.CH_2.CH_3$. — This acid is prepared by oxidation of active amyl alcohol. Although the alcohol turns the plane of polarization to the left, the acid turns it to the right. The alcohol is said to be *lævo-rotatory*, and the acid *dextro-rotatory*.

---

The higher acids of the series are, for the most part, found in various fats. They are difficultly soluble in water. The highest members are solids. The two best known, because occurring in largest quantity, are *palmitic* and *stearic acids*. These are contained in combination with the alcohol, glycerin, in all the common fats. The fats will be treated of under the head of Glycerin.

**Palmitic acid,** $C_{15}H_{31}.CO_2H$, may be made by saponifying many fats, but especially *palm-oil*, from which it is obtained mixed with only one other acid.

It crystallizes in needles which melt at 62°.

**Stearic acid,** $C_{17}H_{35}.CO_2H$, is the acid contained in that *particular* fat known as *stearin*. The so-called "stearin candles" are really made of a mixture of palmitic and stearic acids, and from them stearic acid can be separated in pure form by long-continued fractional crystallization from ethĕr and alcohol.

It crystallizes from alcohol in needles or laminæ which melt at 69°.

**Soaps.** — In speaking of the decompositions of ethereal salts by boiling with alkalies, it was stated that this process is called saponification because it is best exemplified in the manufacture of soaps from fats. The fats are themselves rather complicated ethereal salts. When they are boiled with an alkali, as caustic soda, the alcohol is liberated, and the alkali salts of the acids are formed. *These salts are the soaps.* They are in solution after the process of saponification is completed, and may be separated by adding a solution of common salt, in which they are insoluble.

**Experiment 33.** In an iron pot boil about 100g of lard with a solution of caustic soda for two hours. After cooling, add a strong solution of sodium chloride. The soap will separate and rise to the top of the solution, where it will finally solidify. Dissolve some of the soap thus obtained in water, and filter. Add hydrochloric acid, when the free fatty acids, mainly palmitic and stearic acids, will separate as solids, which will rise to the top. The hydrochloric acid simply decomposes the sodium palmitate and stearate, giving free palmitic and stearic acids and sodium chlorides: —

$$\underset{\text{Sodium Palmitate.}}{C_{15}H_{31}.CO_2Na} + HCl = \underset{\text{Palmitic Acid.}}{C_{15}H_{31}.CO_2H} + NaCl,$$

and

$$\underset{\text{Sodium Stearate.}}{C_{17}H_{35}.CO_2Na} + HCl = \underset{\text{Stearic Acid.}}{C_{17}H_{35}.CO_2H} + NaCl.$$

---

The remaining derivatives of the higher members of the paraffin series include the ethers, ketones, ethereal salts, mercaptans, sulphur ethers, sulphonic acids, cyanides and isocyanides, cyanates and isocyanates, sulpho-cyanates and iso-sulpho-cyanates, substituted ammonias and analogous compounds, metal derivatives, and nitro-derivatives.

A great many substances belonging to these classes, and containing residues of the higher hydrocarbons, have been prepared and studied; but, in the main, they so closely resemble the simpler substances which have already been described that we would gain nothing by taking them up here individually. The student, however, is earnestly advised to apply the principles discussed in the first part of the book to a few other cases. Thus, let him take propane and butane, and, not only write the formulas of the derivatives which may be obtained from them, but, above all, write the equations representing the action involved in their preparation, and the transformations of which they are capable.

## POLYACID ALCOHOLS AND POLYBASIC ACIDS.

### 1. Di-acid Alcohols.

The alcohols thus far considered are of the simplest kind. They correspond to the simplest metallic hydroxides, as potassium hydroxide, KOH. Just as these simplest metallic hydroxides are called *mon-acid bases*, so the simplest alcohols are called *mon-acid alcohols*,[1] expressions which are suggested by the term *mono-basic acid*. But, as is well known, there are metallic hydroxides, like calcium hydroxide, $Ca(OH)_2$, barium hydroxide, $Ba(OH)_2$, etc., which contain two hydroxyls, and are hence known as *di-acid bases;* and so, too, there are *di-acid alcohols* which bear to the mon-acid alcohols the same relation that the di-acid bases bear to the mon-acid bases. Only one alcohol of this kind, derived from the paraffin hydrocarbons, is well known.

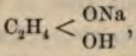
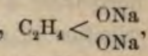
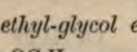
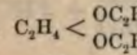
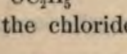
**Ethylene alcohol or glycol, $C_2H_6O_2[C_2H_4(OH)_2]$.**—Glycol is made by starting with ethylene, a hydrocarbon of the formula

---

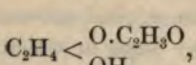
[1] The expression *monatomic* alcohols is used by some writers, but, as it is confusing, it is gradually giving way to the more rational expression above used.

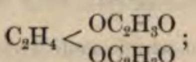
$C_2H_4$. When this is brought together with bromine, the two unite directly, forming *ethylene bromide*, $C_2H_4Br_2$. By replacing the two bromine atoms by hydroxyl, ethylene alcohol or glycol is formed.

It is a colorless, inodorous, somewhat oily liquid, which boils at 197.5°. It has a sweetish taste, and is hence called *glycol* (from γλυκύς, *sweet*). Hence, further, the other alcohols of this series are also called *glycols*.

The derivatives of ethylene alcohol are not as numerous as those of the better known members of the methyl alcohol series, but those which are known are of the same general character. The reactions of the alcohol are the same as those of the mon-acid alcohols, but it presents more possibilities. In most cases in which a mon-acid alcohol yields one derivative, ethylene alcohol yields two. Thus, with sodium, the two compounds, *sodium glycol*,  $C_2H_4<\begin{matrix}ONa\\OH\end{matrix}$, and *di-sodium glycol*,  $C_2H_4<\begin{matrix}ONa\\ONa\end{matrix}$, can be formed; from these, by treating with ethyl iodide, the two ethers, *ethyl-glycol ether*,  $C_2H_4<\begin{matrix}OC_2H_5\\OH\end{matrix}$, and *di-ethyl-glycol ether*,  $C_2H_4<\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}$, are made. By treatment with hydrochloric acid, the chloride,  $C_2H_4<\begin{matrix}Cl\\OH\end{matrix}$, known as *ethylene chlorhydrine* is formed; and this, by treatment with phosphorus trichloride, may be converted into ethylene chloride, $C_2H_4Cl_2$, etc.

Its conduct towards acids is like that of a di-acid base. It forms *neutral* and *alcoholic salts*, of which the acetates may serve as examples. Thus we have the

*Mono-acetate*, 
$$C_2H_4<\begin{matrix}O.C_2H_3O\\OH\end{matrix},$$

and the *Di-acetate*, 
$$C_2H_4<\begin{matrix}OC_2H_3O\\OC_2H_3O\end{matrix};$$

the former still containing alcoholic hydroxyl and corresponding to a basic salt; the latter being a neutral compound.

Under the head of Acetyl Chloride (see p. 62) the action of acetyl chloride upon organic compounds containing oxygen was spoken of as affording a convenient method of determining whether a given substance is an alcohol or not. It is plain that, as the reaction which takes place between a mon-acid alcohol and acetyl chloride, and which is represented by the equation

$$R.OH + C_2H_3OCl = R.OC_2H_3O + HCl,$$

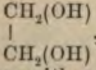
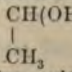
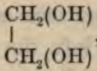
is due to the presence of alcoholic hydroxyl, the reaction must be repeated for every alcoholic hydroxyl contained in the compound; or, at least, this result would be expected. As a matter of fact the reaction is thus repeated for every alcoholic hydroxyl present. Hence, by treating an oxygen derivative with acetyl chloride, we can not only determine whether the derivative is an alcohol or not, but also, if it is an alcohol, whether it is mon-acid or di-acid, etc. Thus, suppose we treat ethylene alcohol with acetyl chloride. This reaction takes place, —

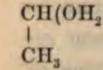
$$C_2H_4(OH)_2 + 2\,C_2H_3OCl = C_2H_4 < \begin{matrix} OC_2H_3O \\ OC_2H_3O \end{matrix} + 2\,HCl;$$

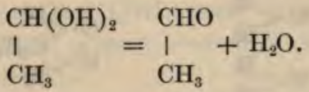
and a body, which analysis shows to have the composition represented by the formula

$$C_6H_{10}O_4 \left( = C_2H_4 < \begin{matrix} OC_2H_3O \\ OC_2H_3O \end{matrix} \right),$$

is formed. Such a body could only be formed by the introduction of two acetyl groups into the alcohol, and we therefore conclude that the original substance is a *di-acid alcohol.*

There are two ways in which the structure of a compound of the formula $C_2H_4(OH)_2$ may be represented. They are, — (1)  $\begin{matrix} CH_2(OH) \\ | \\ CH_2(OH) \end{matrix}$, in which each hydroxyl is represented in combination with a different carbon atom; and (2)  $\begin{matrix} CH(OH)_2 \\ | \\ CH_3 \end{matrix}$, in which *both hydroxyls* are represented in combination with the same carbon atom. The question at once suggests itself, to which of these formulas does ethylene alcohol correspond? To answer this question, we must recall what was said regarding the two dichlor-ethanes, known as *ethylene chloride* and *ethylidene chloride.* The former of these corresponds to the formula $CH_2Cl.CH_2Cl$, while the latter, which is formed from aldehyde by replacing the carbonyl oxygen by two chlorine atoms, is represented by the formula $CHCl_2.CH_3$. When the chlorine atoms of ethylene chloride are replaced by hydroxyl, ethylene alcohol is produced. Hence, the alcohol has the formula  $\begin{array}{l}CH_2(OH)\\ |\\ CH_2(OH)\end{array}$, or each of the hydroxyls is in combination with a different carbon atom.

All attempts to make the isomeric di-acid alcohol corresponding to ethylidene chloride, and having both hydroxyls in combination with the same carbon atom, as represented in the formula  $\begin{array}{l}CH(OH_2)\\ |\\ CH_3\end{array}$, have failed. Instead of getting ethylidene alcohol, aldehyde is generally obtained. Aldehyde is ethylidene alcohol minus water: —



$$\begin{array}{l}CH(OH)_2\\ |\\ CH_3\end{array} = \begin{array}{l}CHO\\ |\\ CH_3\end{array} + H_2O.$$

It is believed that one carbon atom cannot, under ordinary circumstances, hold in combination more than one hydroxyl group. If this is true, then ethylidene alcohol cannot be prepared any more than our hypothetical carbonic acid, $CO < {OH \atop OH}$, can be. So, too, the simplest di-acid alcohol conceivable, viz., methylene alcohol, $CH_2(OH)_2$, cannot exist, but would break up, if formed at all, into water and formic aldehyde: —

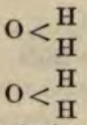
$$CH_2(OH)_2 = H_2O + H.CHO.$$

(See discussion regarding the transformation of alcohol into aldehyde, pp. 64–66.)

Ethyl alcohol, as was pointed out, may be regarded either as ethane in which one hydrogen is replaced by hydroxyl, or as water in which one hydrogen is replaced by the radical $C_2H_5$, or ethyl. Ethyl, like all the radicals contained in the mon-acid alcohols, is *univalent.* It is ethane less one atom of hydrogen, just as methyl is methane less one atom of hydrogen. Each has the power of uniting with one atom of hydrogen, or another univalent element, or of taking the place of one atom of hydrogen.

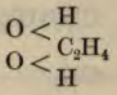
If we take away two atoms of hydrogen from methane and ethane, we have left the residues or radicals $CH_2$ and $C_2H_4$. These can unite with two atoms of hydrogen, or take the place of two atoms of hydrogen, and they are hence called *bivalent radicals.*

Just as ethylene alcohol may be regarded as ethane in which two hydrogen atoms are replaced by hydroxyls, so it may be regarded as water in which the bivalent radical ethylene replaces two hydrogens belonging to two different molecules of water: —



$$\mathrm{O}<\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}$$
$$\mathrm{O}<\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}$$

Two molecules water.



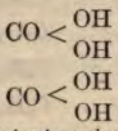
$$\begin{matrix}\mathrm{O}<\mathrm{H}\\ \qquad\mathrm{C_2H_4}\\ \mathrm{O}<\mathrm{H}\end{matrix}$$

Ethylene alcohol.

The higher members of the series of di-acid alcohols will not be considered here.

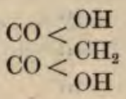
## 2. Bibasic Acids.

Just as there are di-acid alcohols derived from the paraffins, so there are bibasic acids which may also be regarded as derivatives of the paraffins. We have seen that the simplest acids, the monobasic fatty acids, are closely related to formic and carbonic acids; that they may be regarded as derived from the latter by replacement of a hydroxyl by a radical, or as derived from the paraffins by the introduction of the group carboxyl, $CO_2H$. The conditions existing in this group are essential to the acid properties. If two carboxyls be introduced into marsh gas, we would have a substance of the formula $CH_2(CO_2H)_2$, and this is a bibasic acid. It contains two acid hydrogens, and is capable of forming two series of salts, the acid and neutral salts, like other bibasic acids. It may be regarded also as derived from two molecules of carbonic acid by the replacement of two hydroxyls by the bivalent radical $CH_2$: —



$$\begin{array}{l}\mathrm{CO}<\substack{\mathrm{OH}\\ \mathrm{OH}}\\ \mathrm{CO}<\substack{\mathrm{OH}\\ \mathrm{OH}}\end{array}$$

Two molecules carbonic acid.



$$\begin{array}{l}\mathrm{CO}<\substack{\mathrm{OH}\\ \mathrm{CH_2}}\\ \mathrm{CO}<\substack{\\ \mathrm{OH}}\end{array}$$

Bibasic acid.

The general methods of preparation available for the building up of the series of bibasic acids are modifications of those used in making the monobasic acids. They are: —

1. *Oxidation of di-acid primary alcohols.* Just as a mon-acid primary alcohol, $R.CH_2OH$, yields by oxidation a monobasic acid, so a di-acid primary alcohol, $R''(CH_2OH)_2$, yields a bibasic acid, $R''(CO_2H)_2$.

2. *Treatment of the dicyanides,* $R''(CN)_2$, *with caustic alkalies.*

3. *Oxidation of the so-called hydroxy-acids or alcohol acids.* These are compounds which are at the same time alcohol and acid; as, for example, hydroxy-acetic acid, which is acetic acid in which one of the hydrogen atoms of the hydrocarbon residue, methyl, has been replaced by hydroxyl, as represented in the formula $\begin{array}{l}CH_2OH\\ |\\ CO_2H\end{array}$. When this is oxidized, the alcoholic portion, $CH_2OH$, is converted into carboxyl, and a bibasic acid is formed.

4. From the cyanogen derivatives of the monobasic acids, such as cyan-acetic acid, $CH_2<\substack{CN\\ CO_2H}$, by the transformation of the cyanogen group into carboxyl.

### BIBASIC ACIDS, $C_nH_{2-2}O_4$.

| | | |
|---|---|---|
| Oxalic | acid | $(CO_2H)_2$. |
| Malonic | " | $CH_2(CO_2H)_2$. |
| Succinic | " | $C_2H_4(CO_2H)_2$. |
| Pyrotartaric | " | $C_3H_6(CO_2H)_2$. |
| Adipic | " | $C_4H_8(CO_2H)_2$. |
| Pimelic | " | $C_5H_{10}(CO_2H)_2$. |
| Suberic | " | $C_6H_{12}(CO_2H)_2$. |
| Azelaic | " | $C_7H_{14}(CO_2H)_2$. |
| Sebacic | " | $C_8H_{16}(CO_2H)_2$. |
| Brassylic | " | $C_9H_{18}(CO_2H)_2$. |
| Roccellic | " | $C_{15}H_{30}(CO_2H)_2$. |

Of the many acids included in this list only four or five can be said to be well known. We may confine our attention to the first four members.

**Oxalic acid, $C_2H_2O_4[(CO_2H)_2]$.**—In one sense, according to the accepted definition, oxalic acid is not a member of the series with which we are dealing, as it is not derived from a hydrocarbon by replacement of hydrogen by carboxyl; nor is it derived from two molecules of carbonic acid by replacement of two hydroxyls by a bivalent radical. Still it is in other respects so closely allied to the members of the series, and has so many things in common with the other members, that it would be a mere act of pedantry to consider it in any other connection.

Oxalic acid occurs very widely distributed in Nature; as in certain plants of the *oxalis* varieties, in the form of the acid potassium salt; as calcium salt in many plants; in urinary calculi; and as the ammonium salt in guano.

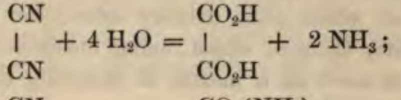
It is formed by the action of nitric acid upon many organic substances, particularly the different varieties of sugar and the so-called carbohydrates, such as starch, cellulose, etc.

**Experiment 34.** In a good-sized flask pour half a litre of ordinary concentrated nitric acid (of specific gravity 1.245) upon 100$^{g}$ of sugar. Heat gently until the reaction begins. Then withdraw the flame, when the oxidation will proceed with some violence, and accompanied by a copious evolution of red fumes. Let it cool, when oxalic acid will crystallize out. Pour off the mother liquor and evaporate somewhat, when more oxalic acid will crystallize out. Recrystallize from water the acid thus obtained, and with the pure substance perform such experiments as will exhibit its properties. For example, (1) Heat a specimen at 100°, and notice loss of water; (2) Heat some in a small flask with sulphuric acid, and prove that both oxides of carbon are formed.

On the large scale, oxalic acid is made by heating wood shavings or saw-dust with caustic potash and caustic soda to 240° to 250°. The mass is extracted with water, and the solution evaporated to crystallization, when sodium oxalate is deposited.

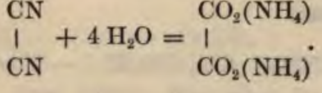
Other methods, which are interesting from a purely scientific stand-point, are the following: —

1. The spontaneous transformation of an aqueous solution of cyanogen: —



$$\begin{array}{l} CN \\ | \\ CN \end{array} + 4\,H_2O = \begin{array}{l} CO_2H \\ | \\ CO_2H \end{array} + 2\,NH_3;$$

or, really,



$$\begin{array}{l} CN \\ | \\ CN \end{array} + 4\,H_2O = \begin{array}{l} CO_2(NH_4) \\ | \\ CO_2(NH_4) \end{array}.$$

2. Treatment of carbon dioxide with sodium: —

$$2\,CO_2 + 2\,Na = C_2O_4Na_2.$$

3. Heating sodium formate: —

$$2\,H.CO_2Na = C_2O_4Na_2 + 2\,H.$$

Oxalic acid crystallizes from water in monoclinic prisms containing two molecules of water ($C_2H_2O_4 + 2\,H_2O$). It loses this water at 100°. It sublimes without decomposition at 150° to 160°, but, if heated higher, it breaks up into carbon monoxide, carbon dioxide, and formic acid:—

$$2\,C_2H_2O_4 = 2\,CO_2 + CO + HCO_2H + H_2O.$$

Sulphuric acid decomposes it into carbon monoxide, carbon dioxide, and water. Heated with glycerin to 100°, carbon dioxide and formic acid are formed (see Formic Acid):—

$$C_2H_2O_4 = CO_2 + H.CO_2H.$$

It is an excellent reducing agent, and is used as a standardizer in preparing solutions of potassium permanganate.

**Experiment 35.** Try the action of a solution of potassium permanganate on a solution of oxalic acid. Why is it best to have the solution of the permanganate acid?

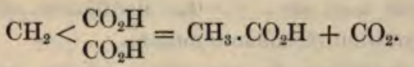
Oxalic acid is an active poison. It is used in calico printing.

*Salts of oxalic acid.* Like all bibasic acids, oxalic acid forms acid and neutral salts with metals. All the salts are insoluble except those containing the alkalies. Among those most common are the *acid potassium salt*, $C_2O_4HK$, which is found in the sorrels or plants of the *oxalis* variety; the *ammonium salt*, $C_2O_4(NH_4)_2$, of which some urinary calculi are formed; and calcium oxalate, $C_2O_4Ca$, which, being insoluble in water and acetic acid, is used as a means of detecting calcium in the presence of magnesium.

**Malonic acid, $C_3H_4O_4[=CH_2(CO_2H)_2]$.**—This acid was first made by oxidation of malic acid (which see), and is hence called *malonic acid*. It can best be made by starting with acetic acid. The necessary steps are: (1) making chlor-acetic acid; (2) transforming chlor-acetic acid into cyan-acetic acid; (3) heating cyan-acetic acid with an alkali.

NOTE FOR STUDENT.—Write the equations representing the three steps mentioned.

It is a solid which crystallizes in laminæ. It breaks up at a temperature above 132°, which is its melting-point, into carbon dioxide and acetic acid: —



$$CH_2 < \begin{matrix} CO_2H \\ CO_2H \end{matrix} = CH_3.CO_2H + CO_2.$$

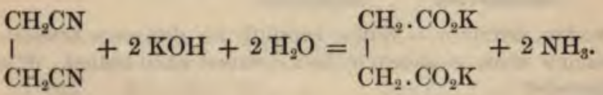
Note for Student. — What simple method for the preparation of marsh gas and other paraffins is this reaction analogous to?

**Succinic acids,** $C_4H_6O_4[= C_2H_4(CO_2H)_2]$. — Considering these acids as derived from ethane by replacing two hydrogens with carboxyl, we see that there may be two corresponding to ethylene and ethylidene chlorides. Two are actually known. One is the well-known succinic acid; the other is called *iso-succinic acid.*

**Succinic acid, Ethylene succinic acid,** $\begin{matrix} CH_2.CO_2H \\ | \\ CH_2.CO_2H \end{matrix}$. — This acid occurs in amber (hence its name, from Lat. *succinum*, amber); in some varieties of lignite; in many plants; and in the animal organism, as in the urine of the horse, goat, and rabbit.

It is formed under many circumstances, especially by oxidation of fats with nitric acid, by fermentation of calcium malate, and, in small quantity, in the alcoholic fermentation of sugar. Among the methods for its preparation are: —

1. Treatment of ethylene cyanide, $\begin{matrix} CH_2.CN \\ | \\ CH_2.CN \end{matrix}$, with a caustic alkali: —



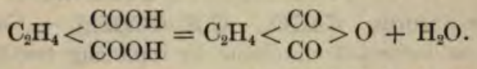
$$\begin{matrix} CH_2CN \\ | \\ CH_2CN \end{matrix} + 2\,KOH + 2\,H_2O = \begin{matrix} CH_2.CO_2K \\ | \\ CH_2.CO_2K \end{matrix} + 2\,NH_3.$$

2. Similarly, by treatment of β-cyan-propionic acid with an alkali. (What is β-cyan-propionic acid?)

3. Reduction of tartaric and malic acids by means of

hydriodic acid. These well-known acids will be shown to be closely related to succinic acid, and the reaction here mentioned will be explained. The methods actually used in the preparation of succinic acid are: (1) the distillation of amber, and (2) the fermentation of calcium malate.

The acid crystallizes in monoclinic prisms, which melt at 180° (try it). It boils at 235°, at the same time giving off water, and being converted into the *anhydride:* —

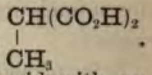


$$C_2H_4 < \begin{matrix} COOH \\ COOH \end{matrix} = C_2H_4 < \begin{matrix} CO \\ CO \end{matrix} > O + H_2O.$$

Among the salts *ferric succinate*, $C_4H_4O_4.Fe(OH)$, is of special interest, as it is entirely insoluble in water, and may therefore be used for the purpose of separating iron from aluminium quantitatively.

**Experiment 36.** Make a neutral solution of ammonium succinate by neutralizing an aqueous solution of the acid, and boiling off all excess of ammonia. Add some of this solution to a solution known to contain aluminium and iron in the ferric state. A brown-red precipitate will be formed. Filter and wash, and examine the filtrate for iron.

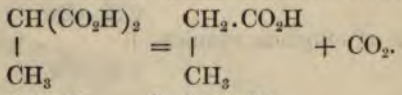
**Isosuccinic acid, Ethylidene succinic acid,**



$$\begin{matrix} CH(CO_2H)_2 \\ | \\ CH_3 \end{matrix}.$$

This acid is made by treating α-cyan-propionic acid with an alkali. (What is α-cyan-propionic acid?)

Isosuccinic acid forms crystals which melt at 130°. Heated to 150° it breaks up into propionic acid and carbon dioxide: —

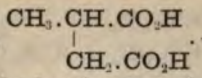


$$\begin{matrix} CH(CO_2H)_2 \\ | \\ CH_3 \end{matrix} = \begin{matrix} CH_2.CO_2H \\ | \\ CH_3 \end{matrix} + CO_2.$$

Isosuccinic acid. Propionic acid.

NOTE FOR STUDENT. — Notice carefully the difference between the two succinic acids, as shown by their conduct when heated. What is the difference?

**Acids of the formula $C_5H_8O_4[=C_3H_6(CO_2H)_2]$.** — Four acids of the formula $C_5H_8O_4$ are known, only one of which, however, need be considered here. This is, —



**Pyrotartaric acid,** $\begin{array}{l}CH_3.CH.CO_2H\\ \quad\quad\;\, |\\ \quad\;\; CH_2.CO_2H\end{array}$. — As the name indicates, this acid is made by heating tartaric acid. The reactions which take place are complicated, and cannot well be represented by equations. The reactions which point to the above formula are also comparatively complicated, and their discussion at this time would tend only to confuse the student.

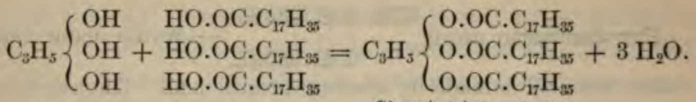
## TRI-ACID ALCOHOLS.

The existence of mon-acid alcohols corresponding to the mon-acid bases, like potassium hydroxide, and of di-acid alcohols corresponding to the di-acid bases, like calcium hydroxide, suggests the possible existence of *tri-acid alcohols* corresponding to tri-acid bases, like ferric hydroxide. There is only one alcohol of this kind derived from the paraffin hydrocarbons that is at all well known. This is the common substance glycerin.

**Glycerin, $C_3H_8O_3$.** — As has been stated repeatedly, glycerin occurs very widely distributed as the alcoholic or basic constituent of the fats. The acids with which it is in combination are mostly members of the fatty acid series, though one, viz., *oleïc acid*, which is found frequently, is a member of another series. Besides oleïc acid, the two acids most frequently met with in fats are palmitic and stearic acids. When a fat is saponified with caustic potash, it yields free glycerin and the potassium salts of the acids. The reactions in the case of the glycerin compounds of palmitic and stearic acids are these: —

*Formation.*

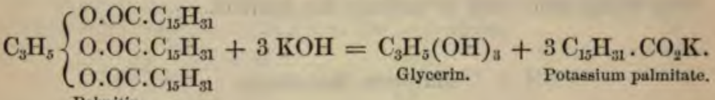
$$\underset{\text{Glycerin.}}{C_3H_5\left\{\begin{array}{l}OH\\OH\\OH\end{array}\right.} + \underset{\text{Palmitic acid.}}{\begin{array}{l}HO.OC.C_{15}H_{31}\\HO.OC.C_{15}H_{31}\\HO.OC.C_{15}H_{31}\end{array}} = \underset{\text{Glycerin tri-palmitate, or Palmitin.}}{C_3H_5\left\{\begin{array}{l}O.CO.C_{15}H_{31}\\O.CO.C_{15}H_{31}\\O.CO.C_{15}H_{31}\end{array}\right.} + 3\,H_2O.$$



$$C_3H_5\left\{\begin{array}{l}OH\\OH\\OH\end{array}\right. + \begin{array}{l}HO.OC.C_{17}H_{35}\\HO.OC.C_{17}H_{35}\\HO.OC.C_{17}H_{35}\end{array} = C_3H_5\left\{\begin{array}{l}O.OC.C_{17}H_{35}\\O.OC.C_{17}H_{35}\\O.OC.C_{17}H_{35}\end{array}\right. + 3\,H_2O.$$

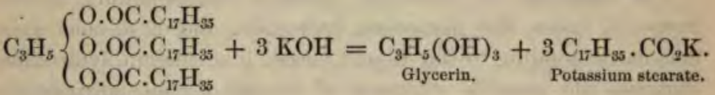
Glycerin. Stearic Acid. Glycerin tri-stearate, or Stearin.

*Saponification.*



$$C_3H_5\left\{\begin{array}{l}O.OC.C_{15}H_{31}\\O.OC.C_{15}H_{31}\\O.OC.C_{15}H_{31}\end{array}\right. + 3\,KOH = C_3H_5(OH)_3 + 3\,C_{15}H_{31}.CO_2K.$$

Palmitin. Glycerin. Potassium palmitate.



$$C_3H_5\left\{\begin{array}{l}O.OC.C_{17}H_{35}\\O.OC.C_{17}H_{35}\\O.OC.C_{17}H_{35}\end{array}\right. + 3\,KOH = C_3H_5(OH)_3 + 3\,C_{17}H_{35}.CO_2K.$$

Stearin. Glycerin. Potassium stearate.

The fats are also decomposed by superheated steam, yielding free glycerin and the free acids, and this method is used on the large scale, a little lime being added to facilitate the process. Lead oxide decomposes fats yielding a mixture of glycerin and the lead salts of the acids. The mixture is known in medicine as "lead plaster."

Glycerin is formed in small quantity by the alcoholic fermentation of sugar.

It has been made synthetically from propylene chloride, $C_3H_6Cl_2$. The necessary steps are: (1) treatment with chlorine, giving $C_3H_5Cl_3$; (2) treatment of the tri-chlorine derivative with water, thus replacing the three chlorine atoms by hydroxyl.

Glycerin is a thick colorless liquid, with a sweetish taste (compare with glycol). It mixes with alcohol and water in all proportions. It attracts moisture from the air. At low temperatures it solidifies, forming deliquescent crystals which melt at 17°. Under diminished pressure it can be distilled; but, if heated to its boiling-point under the ordinary atmospheric pressure it undergoes decomposition. It is volatile with water vapor.

**Experiment 37.** Heat a little glycerin in a dry vessel, and try to boil it. What evidence have you that it undergoes decomposition? Put $20^{cc}$ to $30^{cc}$ glycerin in $400^{cc}$ to $500^{cc}$ water in a flask; connect with a condenser, and boil. Prove that glycerin passes over with the water vapor.

The reactions of glycerin all clearly lead to the conclusion that it is a tri-acid alcohol.

(1) The three hydroxyl groups can be replaced successively by chlorine, giving the compounds, —

$$\textit{Chlorhydrin}, \quad C_3H_5\left\{\begin{matrix} Cl \\ (OH)_2 \end{matrix}\right. ;$$

$$\textit{Dichlorhydrin}, \quad C_3H_5\left\{\begin{matrix} Cl_2 \\ OH \end{matrix}\right. ;$$

and *Trichlorhydrin*, $C_3H_5Cl_3$,

which last compound is propane in which three hydrogen atoms are replaced by chlorine, or trichlorpropane.

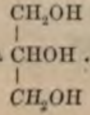
(2) It forms three classes of ethereal salts containing one, two, and three acid residues respectively. For example, with acetyl chloride these reactions take place: —

$$1.\ C_3H_5\left\{\begin{matrix} OH \\ OH \\ OH \end{matrix}\right. + C_2H_3O.Cl = C_3H_5\left\{\begin{matrix} O.C_2H_3O \\ OH \\ OH \end{matrix}\right. + HCl.$$

$$2.\ C_3H_5\left\{\begin{matrix} OH \\ OH \\ OH \end{matrix}\right. + 2\,C_2H_3OCl = C_3H_5\left\{\begin{matrix} OC_2H_3O \\ OC_2H_3O \\ OH \end{matrix}\right. + 2\,HCl.$$

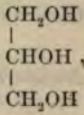
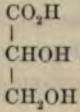
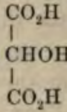
$$3.\ C_3H_5\left\{\begin{matrix} OH \\ OH \\ OH \end{matrix}\right. + 3\,C_2H_3OCl = C_3H_5\left\{\begin{matrix} OC_2H_3O \\ OC_2H_3O \\ OC_2H_3O \end{matrix}\right. + 3\,HCl.$$

In regard to the relations of the hydroxyl groups to the parts of the radical $C_3H_5$, we have very little experimental evidence, though it appears highly probable that each hydroxyl is in combination with a different carbon atom as represented in the formula



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}.$$

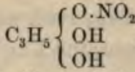
In the first place, we have seen above that compounds containing two hydroxyls in combination with the same carbon are not readily formed, if they are formed at all, and we have had some reason for concluding that this kind of combination is impossible. It would follow from this that the simplest tri-acid alcohol must contain at least three atoms of carbon, just as the simplest di-acid alcohol must contain at least two atoms of carbon. We have seen that the simplest tri-acid alcohol known does contain three atoms of carbon.

Further, if the formula of glycerin is  $\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$, it contains two primary alcohol groups, $CH_2OH$, and we have seen that this group is converted into carboxyl under the influence of oxidizing agents. Therefore, we would expect by oxidizing glycerin to get products of the formulas,  $\begin{array}{c}CO_2H\\ |\\ CHOH\\ |\\ CH_2OH\end{array}$, and  $\begin{array}{c}CO_2H\\ |\\ CHOH\\ |\\ CO_2H\end{array}$. Such products actually are obtained, the first being *glyceric acid* (which see), and the second *tartronic acid* (which see).

Just as ethyl alcohol is regarded as water in which one hydrogen is replaced by the univalent radical $C_2H_5$, as $\left.\begin{array}{c}C_2H_5\\ H\end{array}\right\}O$; and glycol is regarded as water in which two hydrogen atoms of two molecules of water are replaced by the bivalent radical $C_2H_4$, as $C_2H_4\begin{array}{l}\overset{H}{>}O\\ \underset{H}{>}O\end{array}$; so also glycerin may be regarded as water in which three hydrogen atoms of three molecules are replaced by the *trivalent radical* $C_3H_5$, thus: —

$$\begin{array}{c}H.OH\\ H.OH\\ H.OH\end{array} \qquad\qquad C_3H_5\left\{\begin{array}{l}OH\\ OH.\\ OH\end{array}\right.$$

*Three molecules water.* Glycerin.

**Ethereal salts of glycerin.** — Among the important ethereal salts of glycerin are the *nitrates*. Two of these are known; viz., the *mono-nitrate*,  $C_3H_5\left\{\begin{array}{l}O.NO_2\\ OH\\ OH\end{array}\right.$, and the **tri-nitrate,** $C_3H_5(ONO_2)_3$, the latter being the chief constituent of **nitro-glycerin.** Nitro-glycerin is prepared by treating glycerin with a mixture of concentrated sulphuric and nitric acids. It is a pale yellow oil which is insoluble in water. At −20° it crystallizes in long needles. It explodes very violently by concussion. It may be burned in an open vessel, but if heated above 250° it explodes. *Dynamite* is infusorial earth impregnated with nitro-glycerin. Nitro-glycerin is the active constituent of a number of explosives.

**Fats.** — The relation of the fats to glycerin has already been stated. Here it will be necessary only to mention the composition and characteristics of some of the more common fats.

Most fats are mixtures of the three neutral ethereal salts which glycerin forms with palmitic, stearic, and oleïc acids, and which are known by the names *palmitin*, *stearin*, and *oleïn*. *Oleïn* is liquid, and the other two fats are solids, stearin having the higher melting-point. Therefore, the larger the proportion of oleïn contained in a fat the softer it is, while the greater the proportion of stearin the higher its melting-point. Among the fats which are particularly rich in stearin may be mentioned *mutton tallow*, *beef tallow*, and *lard*. *Human fat* and *palm oil* are particularly rich in palmitin. *Sperm oil* and *cod-liver oil* are rich in oleïn.

**Butter** consists of ethereal salts of glycerin and the following acids: myristic, palmitic, and stearic acids, which are not volatile, and butyric, caproïc, caprylic, and capric acids, which are volatile with water vapors. All the acids mentioned are members of the fatty acid series. Some of these acids are soluble and some are insoluble in water. The percentage of insoluble fatty acids contained in butter has been found to be 88 per cent. As the proportion of insoluble fatty acids contained in artificial butters, such as the so-called *oleo-margarin*, is greater than that contained in butter, it is not a difficult matter to distinguish between the two by determining the amount of these acids contained in them.

## TRI-BASIC ACIDS.

There is but one acid to be considered under this head. It is, —

**Tri-carballylic acid, $C_3H_5(CO_2H)_3$.** — This acid may be made from trichlorhydrin, $C_3H_5Cl_3$ (which see), by replacing the chlorine by cyanogen, and heating the *tricyanhydrine* thus obtained with an alkali. It may be made also by treating aconitic acid (which see) with nascent hydrogen.

It crystallizes from water in rhombic prisms which melt at 157° to 158°.

## TETR-ACID ALCOHOLS.

**Erythrite, $C_4H_{10}O_4[=C_4H_6(OH)_4]$.** — This substance occurs in one of the algæ (*Protococcus vulgaris*) and in several lichens. It crystallizes from water in quadratic prisms. It has a very sweet taste. The fact that the simplest tetr-acid alcohol contains four atoms of carbon should be noted specially.

There is no *tetra-basic acid* derived from the hydrocarbons of the paraffin series.

## PENT-ACID ALCOHOLS.

Only one substance need be considered under this head, and even this one is rare. It is, —

**Quercite, $C_6H_7(OH)_5$.** — Quercite is formed in acorns. It crystallizes in prisms from its solutions in water.

No *penta-basic acid* belonging to this series is known.

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### HEX-ACID ALCOHOLS.

There are two isomeric hex-acid alcohols known. Both are derived from hexane, and have the composition represented by the formula $C_6H_8(OH)_6$. It will be noticed that these *hex-acid alcohols* contain *six carbon atoms* each.

**Mannite, $C_6H_8(OH)_6$.** — Mannite is widely distributed in the vegetable kingdom. It occurs most abundantly in manna,[1] which is the partly dried sap of the manna-ash (*Fraxinus ornus*). It is obtained from incisions in the bark of the tree.

Mannite is formed in the lactic acid fermentation of sugar. It is formed also by the action of nascent hydrogen on glucose and cellulose, or on inverted cane sugar. *This indicates a close relationship between the sugars and mannite.* Mannite crystallizes in needles, or rhombic prisms, which are easily soluble in water and in alcohol. It has a sweet taste.

Nitric acid converts mannite into *saccharic acid* (which see). When boiled with concentrated hydriodic acid, it is converted into secondary hexyl iodide, $C_6H_{13}I$.

**Mannite hexa-nitrate (nitro-mannite), $C_6H_8(O.NO_2)_6$,** is formed by treating mannite with a mixture of concentrated sulphuric and nitric acids. It is a solid substance and is very explosive. (Analogy with nitro-glycerin.)

**Mannite hex-acetate, $C_6H_8(O.C_2H_3O)_6$,** is formed by treating mannite with *acetic anhydride.* Its formation, as well as that of the hexa-nitrate, shows that mannite is a hex-acid alcohol. For the purpose of making the acetates, acetic anhydride is sometimes used instead of acetyl chloride. In some cases in which the latter will not work, the former answers very well. Hence acetic anhydride has come into use as a reagent, which enables us to decide whether a substance under examination is or is not an alcohol; and, if it is, to which class (whether mon-acid, di-acid, tri-acid, etc.) it belongs.

---

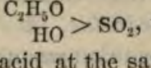
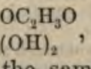
[1] The manna of the Scriptures was obtained from the branches of *Tammarix gallica.* It contained no mannite, but a substance of similar properties.

**Dulcite, $C_6H_8(OH)_6$.**—This occurs in a kind of manna obtained in Madagascar, the source of which, however, is unknown. It is formed by treating sugar of milk or galactose with nascent hydrogen (compare with mannite in this respect).

Dulcite crystallizes in monoclinic prisms; easily soluble in water and in alcohol.

Nitric acid oxidizes dulcite, forming *mucic acid* (which see), isomeric with saccharic acid, which is formed from mannite. Like mannite, when boiled with hydriodic acid it yields secondary hexyl iodide, $C_6H_{13}I$. With acetic anhydride it yields *dulcite hex-acetate*, $C_6H_8(O.C_2H_3O)_6$.

There are no *hexa-basic acids* known belonging to this series.

Neither alcohols nor acids are known containing more than six alcoholic or acid groups. We have, therefore, completed an account of the alcohols, acids, aldehydes, ethers, etc., derived from the paraffin series of hydrocarbons. But we are not yet prepared to pass on to the next series of hydrocarbons. The compounds which up to this time have been considered belong to distinct classes. Each one, with very few exceptions, is either an alcohol or an acid, an aldehyde or a ketone, etc. The few exceptions referred to are the acid ethereal salts, such as ethyl-sulphuric acid,  $\begin{matrix} C_2H_5O \\ HO \end{matrix} > SO_2$, which may be regarded as both ethereal salt and acid at the same time, and the alcoholic ethereal salts, corresponding to basic salts; such, for example, as *glycerin mon-acetate*,  $C_3H_5 \left\{ \begin{matrix} OC_2H_3O \\ (OH)_2 \end{matrix} \right.$, which may be regarded as *ethereal salt* and alcohol at the same time. Such compounds *may be called mixed compounds.*

## CHAPTER X.

## MIXED COMPOUNDS. — DERIVATIVES OF THE PARAFFINS.

UNDER this head are included such compounds as belong at the same time to two or more of the chief classes already considered. Thus, there are substances which are at the same time alcohols and acids. There are others which are at the same time alcohols and aldehydes, alcohols and ketones, acids and ketones, etc. Fortunately, for our purpose, the number of compounds of this kind actually known is comparatively small, though among them are many of the most important natural compounds of carbon. The first class which presents itself is that of the *alcohol acids* or *acid alcohols;* that is, substances which combine within themselves the properties of both alcohol and acid. They are commonly called *oxy-acids* or *hydroxy-acids.*

### HYDROXY-ACIDS, $C_nH_{2n}O_3$.

These acids may be regarded either as monobasic acids into which one alcoholic hydroxyl has been introduced, or as monacid alcohols into which one carboxyl has been introduced. As their acid properties are more prominent than the alcoholic properties, they are commonly referred to the acids. Running parallel, then, to the series of fatty acids, we may look for a series of hydroxy-acids, each of which differs from the corresponding fatty acid by one atom of oxygen, or by containing one hydroxyl in the place of one hydrogen, thus: —

| | Fatty acids. | Hydroxy-acids. |
|---|---|---|
| Formic acid . . . | $H.CO_2H$ | $HO.CO_2H$. |
| Acetic acid . . . | $CH_3.CO_2H$ | $CH_2<\genfrac{}{}{0pt}{}{OH}{CO_2H}$. |
| Propionic acid . . | $C_2H_5.CO_2H$ | $C_2H_4<\genfrac{}{}{0pt}{}{OH}{CO_2H}$. |
| | etc. | etc. |

The first member of the series, which by analogy would be called *hydroxy-formic acid*, is nothing but our ordinary hypothetical carbonic acid. Although its relation to formic acid is the same as that of the next member of the series to acetic acid, it certainly has no properties in common with the alcohols; but, owing to its peculiar structure, it is a bibasic acid which the other members of the series are not. Nevertheless, it may be referred to here for the sake of a few of its derivatives, which are somewhat allied to those of the hydroxy-acids proper.

**Carbonic acid, $H_2CO_3\left(CO<\genfrac{}{}{0pt}{}{OH}{OH}\right)$.**—It is believed that this body exists in solutions of carbon dioxide in water. All that is known about it is that it is a feeble bibasic acid, and breaks up into water and carbon dioxide whenever it is set free from its salts. We have seen that this instability is generally met with in compounds containing two hydroxyls in combination with one carbon atom.

Among the derivatives of carbonic acid which may be referred to at this time are the ethereal salts. These may be made:—

1. By treating silver carbonate, $CO<\genfrac{}{}{0pt}{}{OAg}{OAg}$, with the iodides of alcohol radicals; as, for example,—

$$CO<\genfrac{}{}{0pt}{}{OAg}{OAg} + 2\,C_2H_5I = CO<\genfrac{}{}{0pt}{}{OC_2H_5}{OC_2H_5} + 2\,AgI.$$

2. By treating the alcohols with carbonyl chloride, $COCl_2$:—

$$COCl_2 + 2\,C_2H_5OH = CO(OC_2H_5)_2 + 2\,HCl.$$

**Ethyl chlor-carbonate,** $CO<{Cl \atop OC_2H_5}$.—This compound is made by treating alcohol with carbonyl chloride:—

$$COCl_2 + C_2H_5OH = CO<{Cl \atop OC_2H_5} + HCl.$$

It may be regarded as the ethyl salt of mono-chlor-formic acid, $Cl.COOH$; and, properly speaking, should be called *ethyl chlor-formate*.

Carbon bisulphide acts very much like carbon dioxide towards alkalies and alcohols, and thus a number of ether acids and ethereal salts containing sulphur may be made. Thus, when carbon bisulphide is added to a solution of caustic potash in alcohol, a potassium salt of the formula $CS<{OC_2H_5 \atop SK}$ is formed. This is called *potassium xanthogenate*. The free xanthogenic acid is very unstable, breaking up into alcohol and carbon bisulphide. The formation of the salt is represented by the following equation:—

$$CS_2 + KOH + C_2H_5OH = CS<{OC_2H_5 \atop SK} + H_2O.$$

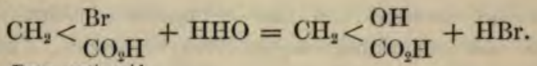
A similar salt made from ordinary amyl alcohol has been used for the purpose of destroying *phylloxera*, the insect, which is so destructive to grape-vines, particularly in the wine districts of France.

*General methods for the preparation of hydroxy-acids.* The methods available for making the hydroxy-acids are modifications of those used for making alcohols and acids.

Starting from a mon-acid alcohol, we may make a hydroxy-acid by the same methods which we used in making an acid from a hydrocarbon. Suppose, for example, that we are to make acetic acid from marsh gas. The reactions which we make use of are: (1) the preparation of a halogen derivative; (2) conversion of the halogen derivative into the cyanogen derivative; and (3) conversion of the cyanogen derivative into the acid. We describe the results of these operations by saying that we have introduced carboxyl. By similar operations we may introduce carboxyl into methyl alcohol, and the product is hydroxy-acetic acid.

It is, however, generally better to start from an acid and introduce hydroxyl. This may be done in several ways: —

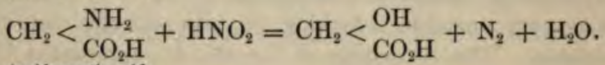
1. By treating a halogen derivative of an acid with water or silver hydroxide: —



$$CH_2<\begin{matrix}Br\\CO_2H\end{matrix} + HHO = CH_2<\begin{matrix}OH\\CO_2H\end{matrix} + HBr.$$

Brom-acetic acid.

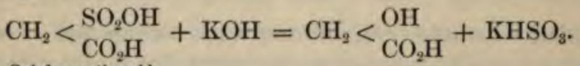
2. By treating an *amido derivative* of an acid with nitrous acid (see page 98): —



$$CH_2<\begin{matrix}NH_2\\CO_2H\end{matrix} + HNO_2 = CH_2<\begin{matrix}OH\\CO_2H\end{matrix} + N_2 + H_2O.$$

Amido-acetic acid.

3. By treating a *sulphonic-acid* derivative of an acid with caustic potash: —



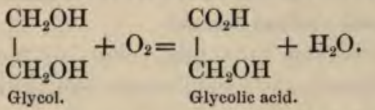
$$CH_2<\begin{matrix}SO_2OH\\CO_2H\end{matrix} + KOH = CH_2<\begin{matrix}OH\\CO_2H\end{matrix} + KHSO_3.$$

Sulpho-acetic acid.

The first two of these reactions have been described and mentioned as affording methods for the introduction of hydroxyl into hydrocarbons. It will be seen that the only difference between the reactions used in making alcohols and those used in making hydroxy-acids is that in one case we start from the hydrocarbons, while in the other we start from the acids.

**Glycolic acid, hydroxy-acetic acid, oxy-acetic acid,** $C_2H_4O_3\left(=CH_2<\begin{matrix}OH\\CO_2H\end{matrix}\right)$. — Glycolic acid is found in nature in unripe grapes, and in the leaves of the wild grape (*Ampelopsis hederacea*).

It may be made from glycocoll, which is amido-acetic acid (see reaction 2, above), from brom- or chlor-acetic acid and water (see reaction 1, above), by the oxidation of glycol:—

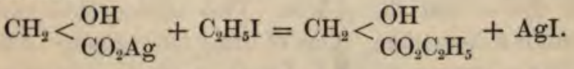


$$\underset{\text{Glycol.}}{\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}} + O_2 = \underset{\text{Glycolic acid.}}{\begin{array}{l}CO_2H\\ |\\ CH_2OH\end{array}} + H_2O.$$

This consists in transforming one of the primary alcohol groups, $CH_2OH$, contained in glycol into carboxyl. (What would be formed by conversion of both the primary alcohol groups of glycol into carboxyl?) It may also be made by careful oxidation of ethyl alcohol with nitric acid. For this purpose a mixture of alcohol and nitric acid is allowed to stand until no further action takes place.

Glycolic acid forms crystals which are easily soluble in water, alcohol, and ether.

As an acid, glycolic acid forms a series of salts with metals, and ethereal salts with alcohol radicals. The latter, of which ethyl glycolate may be taken as an example, may be made by means of one of the reactions usually employed for making ethereal salts; for example, by treating silver glycolate with ethyl iodide:—

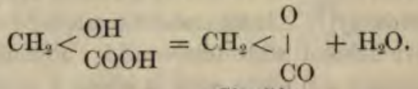


$$CH_2 < \begin{array}{l}OH\\ CO_2Ag\end{array} + C_2H_5I = CH_2 < \begin{array}{l}OH\\ CO_2C_2H_5\end{array} + AgI.$$

In this reaction, as well as in the formation of salts of glycolic acid, the alcoholic hydroxyl remains unchanged.

As an alcohol, glycolic acid forms ethers of which *ethyl-glycolic acid*, $CH_2 < \begin{array}{l}OC_2H_5\\ CO_2H\end{array}$, may serve as an example. It will be seen that this is isomeric with ethyl glycolate. But while the latter has alcoholic properties, the former has acid properties. Ethyl glycolate is a liquid which boils at 160°. Ethyl-glycolic acid is a liquid which boils at 206° to 207°. Finally, as an alcohol, glycolic acid forms ethereal salts, of which acetyl-glycolic acid may serve as an example. This is glycolic acid in which the hydrogen of the hydroxyl is replaced by acetyl, $CH_2<\genfrac{}{}{0pt}{}{O.C_2H_3O}{CO_2H}$, bearing, as will be seen, the same relation to glycolic acid and acetic acid that ethyl acetate, $C_2H_5.O.C_2H_3O$, bears to alcohol and acetic acid.

Glycolic acid and the other acids of the same series lose water when heated, and yield peculiar anhydrides. The product obtained from glycolic acid is known as *glycolide*. It has neither acid nor alcoholic properties, and is, therefore, believed to be derived from glycolic acid as represented in this equation:—



$$CH_2<\genfrac{}{}{0pt}{}{OH}{COOH} = CH_2<\begin{matrix}O\\ |\\ CO\end{matrix} + H_2O.$$

Glycolide.

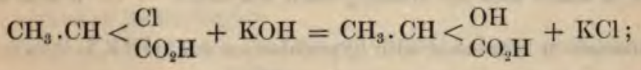
Glycolide is insoluble in cold water. When boiled for a long time with water, it is converted into glycolic acid.

**Lactic acids, hydroxy-propionic acids, oxy-propionic acids, $C_3H_6O_3\left(=C_2H_4<\genfrac{}{}{0pt}{}{OH}{CO_2H}\right)$.** — In speaking of propionic acid, it was pointed out that two series of substitution-products of the acid are known, which are designated as the $\alpha$- and $\beta$-series. Accordingly we would expect to find two hydroxy-propionic acids, the $\alpha$- and the $\beta$-acid. Two lactic acids have been known for a long time. One of these is *ordinary lactic acid;* the other a variety which is found in flesh, and hence called *sarco-lactic acid*. But, strange to say, a thorough investigation of these two acids has proved that both must be represented by the same structural formula, as both conduct themselves in exactly the same way towards reagents. And, further, one other hydroxy-propionic acid is certainly known, and even a fourth has been described. The facts then are these: three, and probably four, acids are known, all of which are hydroxy-propionic acids. Our theory enables us to foretell the existence of only two. Before discussing this discrepancy let us briefly consider the acids themselves.

1. **Lactic acid, inactive ethylidene-lactic acid, α-hydroxy-propionic acid,** $CH_3.CH<\begin{matrix}OH\\CO_2H\end{matrix}$. — The chief method for making lactic acid consists in the fermentation of sugar by the lactic-acid ferment. This process has already been described under the head of Butyric Acid. It is carried out best by dissolving cane sugar and a little tartaric acid in water; then adding putrid cheese, milk, and zinc carbonate. The object of the zinc carbonate is to prevent the solution from becoming acid, as the presence of free acid is fatal to the ferment. The sugar is converted first into glucose, $C_6H_{12}O_6$; and this then breaks up into lactic acid: —

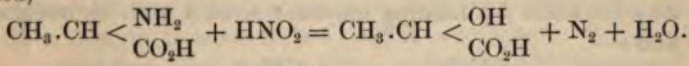
$$C_6H_{12}O_6 = 2\ C_3H_6O_3.$$

It will be remembered that by continued action of the ferment on the lactic acid, butyric acid is formed (see Butyric Acid). Lactic acid may be made also by fermentation of sugar of milk, and is hence contained in sour milk; by boiling α-chlor-propionic acid with alkalies, —



$$CH_3.CH<\begin{matrix}Cl\\CO_2H\end{matrix} + KOH = CH_3.CH<\begin{matrix}OH\\CO_2H\end{matrix} + KCl;$$

and by treating alanine (α-amido-propionic acid) with nitrous acid, —



$$CH_3.CH<\begin{matrix}NH_2\\CO_2H\end{matrix} + HNO_2 = CH_3.CH<\begin{matrix}OH\\CO_2H\end{matrix} + N_2 + H_2O.$$

Lactic acid is a thick liquid which mixes with water and with alcohol in all proportions.

Treated with hydriodic acid, it is reduced to propionic acid. Treated with hydrobromic acid, it yields α-brom-propionic acid.

2. **Sarco-lactic acid, active ethylidene-lactic acid,** $CH_3.CH<\begin{matrix}OH\\CO_2H\end{matrix}$. — This acid occurs in the liquids expressed from meat. It is therefore contained in "extract of meat," and may be obtained most readily from this source.

Its properties are, for the most part, like those of inactive lactic acid, and its conduct towards reagents is in all respects the same. Its salts are somewhat more easily soluble than those of ordinary inactive lactic acid. The chief difference between the two is observed in the action towards polarized light. Active lactic acid turns the plane of polarization to the sight. It is dextro-rotatory. Its salts are all lævo-rotatory. On the other hand, neither inactive lactic acid nor its salts exert any action upon polarized light.[1]

3. **Hydracrylic acid, β-Hydroxy-propionic acid,** $\left.\right\} \begin{array}{l} CH_2OH \\ | \\ CH_2.CO_2H \end{array}.$

Hydracrylic acid is made by boiling β-iodo-propionic acid with water or silver oxide and water: —

$$\begin{array}{l} CH_2I \\ | \\ CH_2.CO_2H \end{array} + HHO = \begin{array}{l} CH_2.OH \\ | \\ CH_2.CO_2H \end{array} + HI.$$

It is made also by starting with ethylene, $\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}$. When this hydrocarbon is treated with hypochlorous acid, HOCl, it is converted into ethylene-chlorhydrine, $\begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array}$ (which see), which may be made by treating ethylene alcohol with hydrochloric acid: —

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + HCl = \begin{array}{l} CH_2Cl \\ | \\ CH_2OH \end{array} + H_2O.$$

By replacing the chlorine with cyanogen, and boiling the cyanhydrine, $\begin{array}{l} CH_2OH \\ | \\ CH_2CN \end{array}$, thus obtained, with an alkali, hydracrylic acid is obtained.

These reactions clearly show that hydracrylic acid is an ethylene compound, and, as it is made from β-iodo-propionic acid by replacing the iodine with hydroxyl, it follows further that the β-substitution-products of propionic acid are ethylene products, and that the α-products are ethylidene products (see p. 131).

---

[1] *See active and inactive amyl alcohols, p. 126.*

Hydracrylic acid is a syrup. Its salts differ markedly from those of the inactive and active lactic acids. When heated, it loses water and is transformed into *acrylic acid*, $CH_2.CH.CO_2H$ (which see).

The difference in conduct between ethylidene-lactic acid and ethylene-lactic acid, when heated, is interesting and suggestive. When ethylidene-lactic acid is heated, both its acid and alcoholic properties are destroyed, both the alcoholic and acid hydroxyls taking part in the reaction. Whereas, when ethylene-lactic acid is heated, only the alcoholic properties are destroyed, the carboxyl remaining intact.

4. **Ethylene-lactic acid.** — A fourth hydroxy-propionic acid, called ethylene-lactic acid, has been described as occurring in meat. There appears, however, to be some little doubt in regard to its existence.

Without reference to the fourth doubtful lactic acid, the fact remains that there are more hydroxy-propionic acids known than our theory can account for. Other cases of this kind are known, and one very marked and especially interesting one will be referred to when tartaric acid is considered. It will be shown that just as there is an active and an inactive lactic acid, so there is an active and an inactive tartaric acid, which conduct themselves in the same way towards reagents, and must hence be represented by the same structural formula.

Apparently we have here to deal with a new kind of isomerism. Bodies may conduct themselves chemically in exactly the same way, and yet differ in some of their physical properties, as in their action towards polarized light. To distinguish this kind of isomerism from ordinary chemical isomerism it is called ***physical isomerism***.

An ingenious hypothesis has been put forward by way of explanation of that particular kind of physical isomerism which shows itself in the action of compounds upon polarized light. It must be remembered that our ordinary formulas have nothing whatever to do with the relations of the atoms and groups in space. They indicate *chemical relations* which are discovered by a study of *chemical reactions*. At present, it is hazardous to indulge in speculations regarding the relations of the parts in space, and, while the hypothesis which is to be explained briefly is ingenious and interesting, the student should be careful not to be carried away by it. He should remember that it is only a thought.

Let us suppose that in a carbon compound one carbon atom is situated at the centre of a tetrahedron, and that the four atoms or groups which it holds in combination are at the angles of the tetrahedron as represented in Fig. 10.

If these groups are all different in kind, and only in this case, it is possible to arrange them in two ways with reference to the carbon atom. The difference between the two arrangements is that which is observed between either one and its reflection in a mirror. Imperfectly the second arrangement of the figure above represented is shown in Fig. 11.

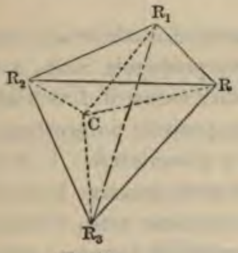


Fig. 10.

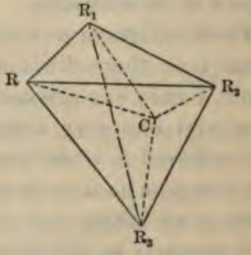
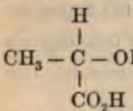


Fig. 11.

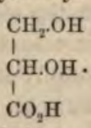
A carbon atom, in combination with four different kinds of atoms or groups, is called an *asymmetrical carbon atom*. *Whenever*, therefore, a compound contains an asymmetrical carbon atom, there are two possible arrangements of its parts in space which correspond to the two complementary tetrahedrons, viz., the *right-handed* and the *left-handed tetrahedron*.

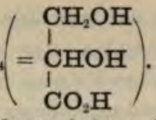
In ethylidene lactic acid there is an asymmetrical carbon atom, as shown by the ordinary formula, which may be written thus:  $CH_3-\underset{CO_2H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-OH$, the central carbon atom appearing in combination with (1) hydrogen, (2) hydroxyl, (3) carboxyl, and (4) methyl. Hence, according to the hypothesis just stated, there ought to be two possible arrangements of the parts of a compound containing this group, one corresponding to the right-handed tetrahedron, the other to the left-handed tetrahedron. Both would be *ethylidene-lactic acids*. Thus we have at least a plausible explanation of the existence of two ethylidene-lactic acids.

NOTE FOR STUDENT. — Has active amyl alcohol an asymmetrical carbon atom?

There are several hydroxy-butyric and valeric acids known, but they need not be considered here.

## HYDROXY-ACIDS, $C_nH_{2n}O_4$.

The acids just considered may be called *monohydroxy-monobasic acids*. Similarly, there are *dihydroxy-monobasic acids*, which may be regarded as derived from the monohydroxy-acids by the introduction of a second hydroxyl. Thus, if into lactic acid, $CH_3.CH<^{CO_2H}_{OH}$, a second hydroxyl be introduced, the product would have the formula  $\begin{array}{c} CH_2.OH \\ | \\ CH.OH \\ | \\ CO_2H \end{array}$. This is the best known dihydroxy-monobasic acid of the paraffin series.

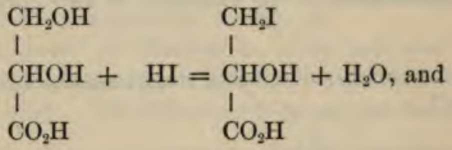


**Glyceric acid,** $C_3H_6O_4 \left( = \begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CO_2H \end{array} \right)$. — This acid has been referred to as the first product of the oxidation of glycerin. It is prepared by allowing glycerin and nitric acid to stand together at the ordinary temperature for some time, and then heating on the water-bath. It may be made also by treating one of the chlor-lactic acids with water.

NOTE FOR STUDENT. — Explain this reaction.

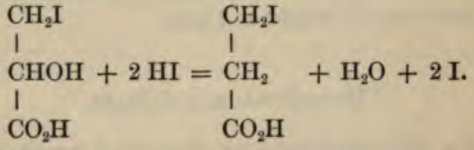
Glyceric acid is a thick syrup which mixes with water and alcohol. When treated with very concentrated hydriodic acid, it is converted into $\beta$-iodo-propionic acid. This conversion involves two reactions: —

(1)



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CO_2H \end{array} + HI = \begin{array}{c} CH_2I \\ | \\ CHOH \\ | \\ CO_2H \end{array} + H_2O, \text{ and}$$

(2)



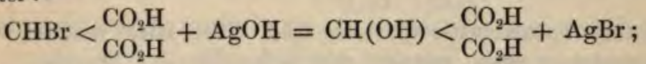
$$\begin{array}{c} CH_2I \\ | \\ CHOH \\ | \\ CO_2H \end{array} + 2\,HI = \begin{array}{c} CH_2I \\ | \\ CH_2 \\ | \\ CO_2H \end{array} + H_2O + 2\,I.$$

## HYDROXY-ACIDS, $C_nH_{2n-2}O_5$.

The acids included under this head are *monohydroxy-dibasic acids.* They bear the same relation to the dibasic acids of the oxalic acid series that the simplest hydroxy-acids bear to the members of the formic acid series. The principal members of this series, and the only ones which will be considered, are tartronic acid and malic acid.

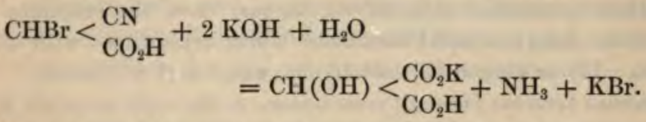
**Tartronic acid,** $C_3H_4O_5\left(=CH(OH)<\genfrac{}{}{0pt}{}{CO_2H}{CO_2H}\right)$. — This acid is prepared by an indirect method from tartaric acid. It may be made, —

(1) By boiling brom-malonic acid with silver oxide and water: —



$$CHBr<\genfrac{}{}{0pt}{}{CO_2H}{CO_2H} + AgOH = CH(OH)<\genfrac{}{}{0pt}{}{CO_2H}{CO_2H} + AgBr;$$

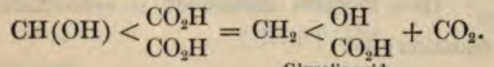
(2) By treating brom-cyan-acetic acid with caustic potash: —



$$CHBr<\genfrac{}{}{0pt}{}{CN}{CO_2H} + 2\ KOH + H_2O$$
$$= CH(OH)<\genfrac{}{}{0pt}{}{CO_2K}{CO_2H} + NH_3 + KBr.$$

Tartronic acid is a solid which crystallizes in prismatic crystals. It is easily soluble in water, alcohol, and ether. It melts at 145°. At 155° it gives off carbon dioxide and water, and is converted into glycolide (which see): —

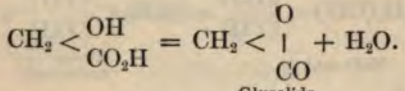
(1)



$$CH(OH)<\genfrac{}{}{0pt}{}{CO_2H}{CO_2H} = CH_2<\genfrac{}{}{0pt}{}{OH}{CO_2H} + CO_2.$$

Glycolic acid.

(2)



$$CH_2<\genfrac{}{}{0pt}{}{OH}{CO_2H} = CH_2<\begin{matrix}O\\ |\\ CO\end{matrix} + H_2O.$$

Glycolide.

Note for Student. — Compare reaction (1) with that which takes place when iso-succinic acid is heated, and note the analogy.

**Hydroxy-succinic acids,** $C_4H_6O_5\left(=C_2H_3(OH)<\genfrac{}{}{0pt}{}{CO_2H}{CO_2H}\right)$. — Three hydroxy-succinic acids have been described, the principal one being ordinary malic acid.

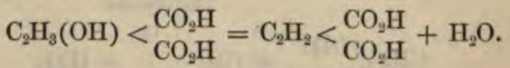
**Malic acid,** $C_4H_6O_5\left(=\begin{matrix}CH(OH).CO_2H\\ |\\ CH_2.CO_2H\end{matrix}\right)$. — This acid is very widely distributed in the vegetable kingdom, as in the berries of the mountain ash, in apples, cherries, etc.

It is best prepared from the berries of the mountain ash which have not quite reached ripeness. The berries are pressed and boiled with milk of lime. The acid passes into solution as the calcium salt, and this is purified by crystallization.

It may be made also by treating aspartic acid, which is amido-succinic acid, $C_2H_3(NH_2) < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$, with nitrous acid, and by treating tartaric acid with hydriodic acid. This latter reaction will be explained when tartaric acid is considered. Tartaric and malic acids are closely related to each other, and both are related to succinic acid, as will appear from the reactions.

Malic acid is a solid substance which crystallizes with difficulty. It is very easily soluble in water and in alcohol. *Its solutions turn the plane of polarization to the right or to the left*, according to the concentration.

When heated it loses water and yields either fumaric or maleic acid (which see), according to the temperature. These acids are isomeric, and both are represented by the formula $C_2H_2 < \begin{matrix} CO_2H \\ CO_2H \end{matrix}$. The reaction mentioned is represented by the following equation: —



$$C_2H_3(OH) < \begin{matrix} CO_2H \\ CO_2H \end{matrix} = C_2H_2 < \begin{matrix} CO_2H \\ CO_2H \end{matrix} + H_2O.$$

Malic acid. Fumaric or maleïc acid.

NOTE FOR STUDENT. — Compare this reaction with that which takes place when hydracrylic is heated, and note the analogy.

When treated with hydriodic acid, malic acid is reduced to succinic acid.

NOTE FOR STUDENT. — Compare this reaction with the conduct of lactic and glyceric acids when treated with hydriodic acid.

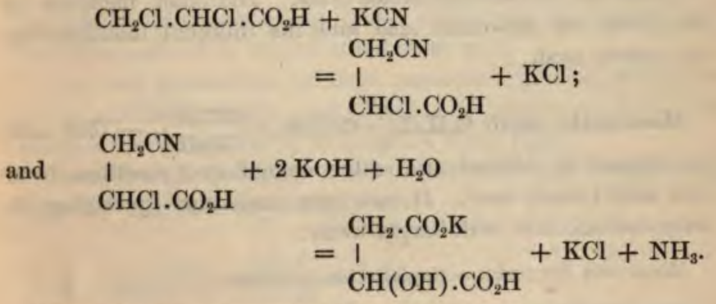
Treated with hydrobromic acid, malic acid is converted into mono-brom-succinic acid.

The reactions just described show clearly that malic acid is hydroxy-succinic acid. Nevertheless, if hydroxy-succinic acid *be made by treating* brom-succinic acid with silver oxide and water, the product is not identical with ordinary malic acid, though the two resemble each other very closely. The acid thus obtained is —

**Inactive malic acid, $C_2H_3(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix}$.** — Inactive malic acid may be made not only by the method first mentioned, but by several others, which indicate that the relation between it and succinic acid is that expressed in the formula given. It, like ordinary malic acid, is unquestionably a hydroxy-succinic acid, and both are derived from ordinary succinic acid.

Other reactions for the preparation of inactive malic acid are, —

(1) By treating dichlor-propionic acid with potassium cyanide, and boiling the product with caustic potash: —

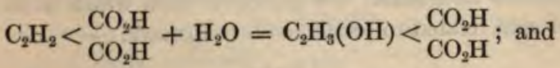


$$CH_2Cl.CHCl.CO_2H + KCN = \begin{matrix}CH_2CN\\ | \\ CHCl.CO_2H\end{matrix} + KCl;$$

and

$$\begin{matrix}CH_2CN\\ | \\ CHCl.CO_2H\end{matrix} + 2\,KOH + H_2O = \begin{matrix}CH_2.CO_2K\\ | \\ CH(OH).CO_2H\end{matrix} + KCl + NH_3.$$

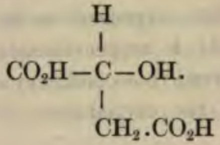
(2) By heating fumaric acid with water: —



$$C_2H_2<\begin{matrix}CO_2H\\CO_2H\end{matrix} + H_2O = C_2H_3(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix}; \text{ and}$$

(3) By reduction of racemic acid with hydriodic acid. Racemic acid has the same composition as tartaric acid. The latter, when treated with hydriodic acid, yields active malic acid.

The properties of inactive malic acid are very much like those of active malic acid. As regards their chemical conduct they are almost identical. The principal difference between them is observed in their conduct towards polarized light. They present a new case of *physical isomerism* of the same kind as that referred to in connection with the lactic acids (which see). The same hypothesis may be applied to this case, for malic acid contains an *asymmetrical carbon atom*, as will be seen by writing the formula in this way:—



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{CO_2H-C-OH.} \\ | \\ \mathrm{CH_2.CO_2H} \end{array}$$

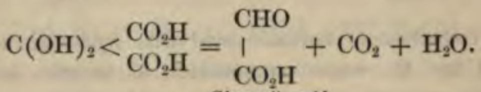
### HYDROXY-ACIDS, $C_nH_{2n-2}O_6$.

These are *di-hydroxy-dibasic acids.* The chief members of the group are mesoxalic acid and the different modifications of tartaric acid.

**Mesoxalic acid,** $C_3H_4O_6\left(=C(OH)_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right)$. — This acid is obtained by indirect and rather complicated reactions from uric acid (which see). It has been made also by boiling di-brom-malonic acid with baryta-water.

NOTE FOR STUDENT. — Explain this reaction.

The acid forms deliquescent needles. When boiled it loses carbon dioxide and water, and glyoxylic acid, which is an aldehyde and acid related to oxalic acid, is formed:—

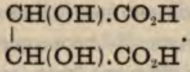


$$\mathrm{C(OH)_2}<\begin{matrix}\mathrm{CO_2H}\\ \mathrm{CO_2H}\end{matrix} = \begin{matrix}\mathrm{CHO}\\ |\\ \mathrm{CO_2H}\end{matrix} + \mathrm{CO_2} + \mathrm{H_2O}.$$

Glyoxylic acid.

This acid affords an example of a very rare condition; viz., the existence of a compound in which two hydroxyls are in *combination with* one and the same carbon atom.

**Di-hydroxy-succinic acids,** $C_4H_6O_6\left(=C_2H_2(OH)_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right)$.

1. **Tartaric acid,** 
$\begin{matrix}CH(OH).CO_2H\\|\\CH(OH).CO_2H\end{matrix}$. — Ordinary tartaric acid occurs very widely distributed in fruits, sometimes free, sometimes in the form of the potassium or calcium salt; as, for example, in grapes, berries of the mountain ash, potatoes, cucumbers, etc., etc.

It may be made by the following methods: —

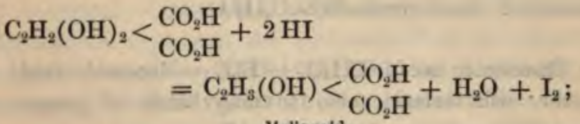
(1) By oxidizing sugar of milk with nitric acid;

(2) Also by oxidizing cane sugar, starch, glucose, and other similar substances.

Tartaric acid is prepared from "tartar," which is impure acid potassium tartrate. When grape juice ferments this salt is deposited. It is purified by crystallization, converted into the calcium salt by treating it with chalk, and the calcium salt then decomposed by means of sulphuric acid.

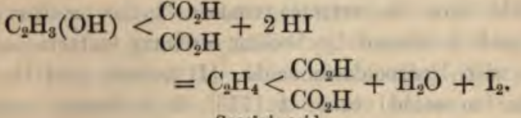
The acid crystallizes in large monoclinic prisms, which are easily soluble in water and alcohol. It melts at 135°. *Its solution turns the plane of polarization to the right.*

Treated with hydriodic acid, tartaric acid yields first malic acid and then ordinary succinic acid: —

(1) 

$$C_2H_2(OH)_2<\begin{matrix}CO_2H\\CO_2H\end{matrix}+2\,HI = C_2H_3(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix}+H_2O+I_2;$$

Malic acid.

(2) 

$$C_2H_3(OH)<\begin{matrix}CO_2H\\CO_2H\end{matrix}+2\,HI = C_2H_4<\begin{matrix}CO_2H\\CO_2H\end{matrix}+H_2O+I_2.$$

Succinic acid.

While malic acid is mono-hydroxy-succinic acid, ordinary tartaric acid appears to be di-hydroxy-succinic acid. But, just as we found that the malic acid prepared from mono-brom-succinic acid is optically inactive, and therefore different from natural, active malic acid, so too it has been found that the tartaric acid prepared from di-brom-succinic acid is optically inactive, and therefore different from ordinary tartaric acid. The relations between the natural and the artificial acids will be considered more fully below.

*Tartrates.* Among the salts the following may be mentioned specially: —

*Mono-potassium tartrate*, $KH.C_4H_4O_6$. This is the chief constituent of *tartar*. In pure form, as used in medicine, it is known under the name of *cream of tartar*.

*Sodium-potassium tartrate*, $KNa.C_4H_4O_6 + 4\ H_2O$. This salt crystallizes very beautifully. It is known as *Rochelle salt* or *Seignette salt*.

*Calcium tartrate*, $Ca.C_4H_4O_6 + 4\ H_2O$. This salt occurs in senna leaves and in grapes. It forms a crystalline powder or rhombic octahedrons.

*Potassium-antimonyl tartrate*, $K(SbO).C_4H_4O_6 + \frac{1}{2}H_2O$. This is known as *tartar emetic*. It is prepared by digesting antimonic oxide with mono-potassium tartrate. It crystallizes in rhombic octahedrons. It loses its water of crystallization at 100°, and at 200 to 220° is converted into an antimony potassium salt of the formula $KSb.C_4H_2O_6$.

2. **Racemic acid, $C_4H_6O_6 + H_2O$.** — Racemic acid occurs, together with tartaric acid, in many kinds of grapes, and, on recrystallizing the crude tartar, acid potassium racemate, being more soluble than the tartrate, remains in the mother liquors. Racemic acid is formed by boiling ordinary tartaric acid with water, or with hydrochloric acid. If tartaric acid be heated with water in sealed tubes at 175°, it is almost completely transformed into racemic acid. It is formed further by oxidation of dulcite, mannite, cane sugar, gum, etc., with nitric acid. *It, together with a third variety of tartaric acid, known as*

*inactive tartaric acid, is formed when bibrom-succinic acid is treated with silver oxide and water.*

Racemic acid differs from tartaric acid in many ways. It crystallizes differently, and contains water of crystallization. It is less soluble than tartaric acid. It produces precipitates in solutions of lime salts, while tartaric acid does not. *Racemic acid is optically inactive*, while tartaric acid is dextro-rotatory. On the other hand, racemic and tartaric acids conduct themselves towards most reagents exactly alike.

Thus far the relations between racemic and tartaric acids appear very much like those which are observed between active and inactive lactic acids and between active and inactive malic acids. But there remains to be described an extremely interesting experiment, which throws new light upon the relations between tartaric and racemic acids.

When a solution of ammonium-sodium racemate,

$$(NH_4)Na.C_4H_4O_6,$$

is allowed to evaporate spontaneously, beautiful large crystals are deposited. On examining these carefully, they are found to be of two kinds. On the crystals of one kind certain hemihedral faces are developed, while on the crystals of the other kind the complementary hemihedral faces are developed; so that if a crystal of one kind is placed in front of a mirror, its reflection will represent the arrangement of the hemihedral faces met with on a crystal of the other kind. The crystals may be separated into *right-handed*, or those which have the right-handed hemihedral faces, and *left-handed*, or those which have the left-handed hemihedral faces.

On separating the acid from the right-handed crystals *it is found to be ordinary dextro-rotatory tartaric acid;* while the acid from the left-handed crystals is an isomeric substance called *lævo-rotatory tartaric acid.* When these two varieties of tartaric acid are brought together in solution, they unite, the action being attended by an elevation of temperature, and *the result is racemic acid.*

We see thus that the *inactive* racemic acid consists of two optically active bodies in combination, one of which, ordinary tartaric acid, is dextro-rotatory, and the other lævo-rotatory.

Inactive malic acid has been resolved into two active varieties, one of which is dextro-rotatory and the other lævo-rotatory. And it is not improbable that inactive lactic acid may be resolved in a similar way.

**Inactive tartaric acid** is very similar to racemic acid. It is formed together with racemic acid by treating dibrom-succinic acid with silver oxide and water. Nothing is known regarding the relation of this substance to the other tartaric acids.

### HYDROXY-ACIDS, $C_nH_{2n-4}O_7$.

These are *mono-hydroxy-tribasic acids.* Citric acid is the only one known.

**Citric acid,** $C_6H_8O_7 + H_2O\left(=C_3H_4(OH)\left\{\begin{array}{l}CO_2H\\CO_2H\\CO_2H\end{array}\right.\right)$. — Citric acid, like malic and tartaric acids, is very widely distributed in nature in many varieties of fruit, especially in lemons, in which it occurs in the free condition. It is found in currants, whortleberries, raspberries, gooseberries, etc., etc.

It is prepared from lemon juice. This is allowed to ferment and is then treated with lime. The lime salt is thus obtained in the form of a precipitate, is collected, and decomposed with sulphuric acid. 100 parts of lemons yield $5\frac{1}{2}$ parts of the acid.

Citric acid crystallizes in rhombic prisms which are very easily soluble in water. The crystallized acid melts at 100°, the anhydrous at 153° to 154°. Heated to 175° it loses water and yields aconitic acid (which see): —

$$C_3H_4(OH)\left\{\begin{array}{l}CO_2H\\CO_2H\\CO_2H\end{array}\right. = \underset{\text{Aconitic acid.}}{C_3H_3\left\{\begin{array}{l}CO_2H\\CO_2H\\CO_2H\end{array}\right.} + H_2O.$$

**Note for Student.** — Compare with formation of acrylic from hydracrylic acid; and of maleïc and fumaric acids from malic acid.

Aconitic acid takes up hydrogen, and is transformed into tricarballylic acid (which see). Thus a clear connection between tricarballylic acid and citric acid is traced, the latter appearing as hydroxy-tricarballylic acid. Citric acid has been made artificially by a somewhat complicated method.

When subjected to dry distillation, citric acid loses both water and carbon dioxide, and yields *citraconic acid*, $C_3H_4 < \substack{CO_2H \\ CO_2H}$, (which see); if heated with water or dilute sulphuric acid to 160° it yields *itaconic acid*, $C_3H_4 < \substack{CO_2H \\ CO_2H}$, (which see).

$$C_3H_4(OH) \left\{ \begin{matrix} CO_2H \\ CO_2H \\ CO_2H \end{matrix} \right. = \underset{\text{Citraconic or itaconic acid.}}{C_3H_4 \left\{ \begin{matrix} CO_2H \\ CO_2H \end{matrix} \right.} + H_2O + C_2O.$$

**Note for Student.** — What relation, as far as composition is concerned, do these two acids of the formula $C_3H_4 \left\{ \begin{matrix} CO_2H \\ CO_2H \end{matrix} \right.$ bear to fumaric and maleïc acids? By distillation of what acid are the two latter formed?

*Citrates.* A few of the salts of citric acid are mentioned: —

*Mono-potassium citrate*, $KH_2.C_6H_5O_7 + 2\,H_2O$;

*Di-potassium citrate*, $K_2H.C_6H_5O_7$;

*Tri-potassium citrate*, $K_3.C_6H_5O_7 + H_2O$. All these potassium salts are easily soluble in water. They are made by mixing citric acid and potassium carbonate in the right proportions.

*Calcium citrate*, $Ca_3(C_6H_5O_7)_2 + 4\,H_2O$. This salt is formed by mixing a citrate of an alkali with calcium chloride. It is more easily soluble in cold than in hot water; hence boiling causes a precipitate in dilute solutions.

*Magnesium citrate*, $Mg_3(C_6H_5O_7)_2 + 14\,H_2O$. This may be made by dissolving magnesia in citric acid. It is used in medicine.

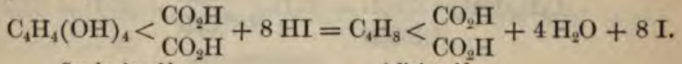
### HYDROXY-ACIDS, $C_nH_{2n-2}O_8$.

There are two acids to be considered under this head. They are isomeric, and both are *tetra-hydroxy-dibasic*.

**Saccharic acid,** $C_6H_{10}O_8\left(=C_4H_4(OH)_4<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right)$.—Saccharic acid is formed by the oxidation of cane sugar, glucose, or sugar of milk with nitric acid.

To prepare it, it is best to treat ordinary sugar with dilute nitric acid. Oxalic acid is formed at the same time.

It is an amorphous mass, which becomes solid only with difficulty. When treated with hydriodic acid it is converted into adipic acid, a member of the oxalic acid series (see table, page 142) :—



$$\underset{\text{Saccharic acid.}}{C_4H_4(OH)_4<\begin{matrix}CO_2H\\CO_2H\end{matrix}} + 8\,HI = \underset{\text{Adipic acid.}}{C_4H_8<\begin{matrix}CO_2H\\CO_2H\end{matrix}} + 4\,H_2O + 8\,I.$$

NOTE FOR STUDENT.—What relations exist between hexane, mannite, adipic acid, and saccharic acid?

**Mucic acid,** $C_6H_{10}O_8\left(=C_4H_4(OH)_4<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right)$.—Mucic acid is formed by oxidizing sugar of milk, the gums, or dulcite, with nitric acid.

It is best prepared by boiling sugar of milk with ordinary nitric acid. Oxalic and tartaric acids are formed at the same time.

It is a crystalline powder which is very difficultly soluble in cold water. Hydriodic acid converts it into adipic acid (see above, under Saccharic Acid).

# CHAPTER XI.

## CARBOHYDRATES.

AMONG the mixed compounds, or compounds which belong at the same time to more than one of the fundamental classes of carbon compounds, are the important bodies called *carbohydrates*. This name was originally given to them because the hydrogen and oxygen which enter into their composition are always present in the proportion to form water, as shown in the formulas for dextrose, $C_6H_{12}O_6$, starch, $C_6H_{10}O_5$, etc. All the compounds belonging to the class of carbohydrates are more or less intimately related to the hex-acid alcohols, as mannite and dulcite, $C_6H_8(OH)_6$. According to their composition, they fall naturally into three groups. These are: —

1. *The glucose group* of the formula $C_6H_{12}O_6$.

The principal members of this group are dextrose or grape sugar, levulose or fruit sugar, and galactose.

2. *The cane sugar group* of the formula $C_{12}H_{22}O_{11}$.

The principal members are cane sugar, sugar of milk, and maltose.

3. *The cellulose group* of the formula $(C_6H_{10}O_5)_x$.

The principal members are cellulose, starch, gum, and dextrin.

### THE GLUCOSE GROUP, $C_6H_{12}O_6$.

**Dextrose, glucose, grape sugar, $C_6H_{12}O_6$.** — Dextrose occurs very widely distributed in the vegetable kingdom, particularly in sweet fruits, in which it is found together with an equivalent quantity of levulose. It is found in honey together with cane sugar and some levulose. It occurs, further, in the blood, in the liver, and in the urine; and, in the disease called

*Diabetes mellitus* the quantity contained in the urine is largely increased, reaching as much as 8 to 10 per cent.

Dextrose is formed from several of the carbohydrates of the formulas $C_{12}H_{22}O_{11}$ and $C_6H_{10}O_5$, by boiling with dilute mineral acids, or by the action of ferments. The formation from cane sugar takes place according to this equation, equivalent quantities of dextrose and levulose being formed: —

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

Starch, cellulose, and dextrin yield dextrose according to this equation: —

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$

Finally, dextrose occurs in nature, in combination with a number of carbon compounds, in the so-called *glucosides*. These break up easily when treated with dilute mineral acids or ferments, and yield dextrose as one of the products (see Glucosides). Examples of the glucosides are amygdalin, æsculin, quercitrin, etc.

Dextrose is prepared on the large scale from corn starch in the United States, and from potato starch in Germany. The transformation is usually effected by boiling with dilute sulphuric acid, though oxalic acid is used to some extent, and phosphoric acid has also been used. The excess of acid is removed by treating the solutions with chalk, and filtering. The filtered solutions are evaporated down either to a syrupy consistency, and sent into the market under the names "glucose," "mixing syrup," etc., or to dryness, the solid product being known in commerce as "grape sugar." By evaporating the solutions down to such a concentration that they contain from 12 to 15 per cent of dextrose, crystals are formed which closely resemble those of cane sugar. They consist of anhydrous grape sugar. Their formation is facilitated by adding a little of the crystallized substance to the concentrated solutions.

*If in the treatment* of starch with sulphuric acid the transformation is not complete, and this is usually the case, the product is a mixture of dextrose, maltose, and dextrin. The longer the action continues, the larger the percentage of dextrose.

Dextrose crystallizes from concentrated solutions, usually in crystalline masses consisting of minute six-sided plates. The mass, as seen in commercial "granulated grape sugar," looks very much like granulated sugar. It crystallizes from alcohol in mono-clinic crystals. It is sweet, but not as sweet as cane sugar. According to the latest estimations, the sweetness of dextrose is to that of cane sugar as 3 to 5. *Its solutions turn the plane of polarization to the right.*

Dextrose is easily oxidized, reducing the salts of silver and copper. When treated with nascent hydrogen, it yields, among other products, mannite and hexyl alcohol. Under the influence of yeast it ferments, yielding mainly alcohol and carbon dioxide. Putrid cheese transforms it first into lactic acid and then into butyric acid by the so-called lactic acid fermentation.

Dextrose forms compounds with metals and salts. Among the better known compounds of this kind are those mentioned below: —

*Sodium dextrose* . . . . $C_6H_{11}O_6 . Na$;
*Sodium chloride dextrose* . $2\,C_6H_{12}O_6 . NaCl + H_2O$;

also, $C_6H_{12}O_6 . NaCl + \frac{1}{2}\,H_2O$, and $C_6H_{12}O_6 . 2\,NaCl$. These compounds, with sodium chloride, crystallize well, and can be easily obtained in pure condition.

*Cupric oxide dextrose* . . $C_6H_{12}O_6 . 5\,CuO$.

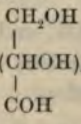
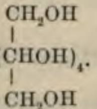
By treatment with acetic anhydride, dextrose yields a product containing five acetyl groups, pent-acetyl-dextrose,

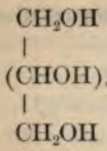
$$C_6H_7(C_2H_3O)_5O_6.$$

Note for Student. — What does the formation of this compound indicate?

It is often important to know the quantity of dextrose contained in a given liquid; as, for example, in the urine in a case of suspected diabetes. For the purpose of making the estimation, advantage is taken of the action of dextrose towards an alkaline solution of copper sulphate. The solution commonly used is that known as *Fehling's solution*. It is prepared by dissolving $34.64^g$ crystallized pure copper sulphate in water, adding a solution of $200^g$ potassium sodium tartrate, and $600^g$ to $700^g$ caustic soda of the specific gravity 1.12, and diluting so that the whole makes one litre.

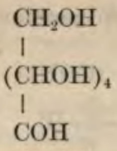
**Experiment 38.** Make half the quantity of Fehling's solution above mentioned, and put in a bottle with a glass stopper. In a test-tube boil about $10^{cc}$ of this solution, and then add a few drops of a dilute solution of glucose. Continue to boil, and add a little more of the glucose solution; and so on, until, on removing the tube from the lamp, a dark-red uniform-looking precipitate settles, leaving the liquid above it perfectly clear and colorless. This precipitate is cuprous oxide. By taking proper precautions, the exact amount of dextrose present in a solution may be estimated in this way.

Regarding the relation between mannite and dextrose we have not much positive knowledge. The fact that dextrose so readily reduces metallic salts, and is converted into mannite by reduction, has led to the belief that it is an aldehyde of mannite, as represented by the formula  $\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ COH \end{array}$, the corresponding alcohol or mannite being  $\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$. While dextrose is converted into mannite by reduction, mannite is not converted into dextrose by oxidation. Both substances are converted into saccharic acid by oxidizing agents, the relations between the three substances being shown by the formulas



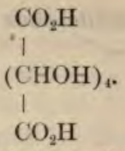
$$\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Mannite.



$$\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ COH \end{array}$$

Dextrose.



$$\begin{array}{c} CO_2H \\ | \\ (CHOH)_4 \\ | \\ CO_2H \end{array}$$

Saccharic acid.

**Levulose (fruit sugar), $C_6H_{12}O_6$.** — As has been stated, levulose occurs together with dextrose, and in equivalent quantities, in fruits; and is formed by the action of dilute mineral acids, or ferments on cane sugar, this last breaking up according to the equation, —

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

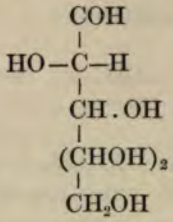
As cane sugar is found in unripe fruits, it is probable that the change represented by the above equation takes place in the process of ripening.

Levulose does not solidify, but forms a thick syrup. It is about as sweet as cane sugar. *It turns the plane of polarization to the left.*

NOTE FOR STUDENT. — What other substances already considered bear to each other the same relations as dextrose and levulose?

It acts towards Fehling's solution the same as dextrose. By nascent hydrogen it is reduced to mannite; and by oxidizing agents it is converted into saccharic acid.

The same arguments which lead to the belief, that dextrose bears to mannite the relation of an aldehyde to an alcohol, lead also to the conclusion that levulose bears the same relation to mannite. At present we do not know what is the cause of the isomerism of dextrose and levulose. Though the same hypothesis that was explained in connection with the two lactic acids may be applied also in this case, as the formula representing dextrose and levulose as aldehydes of mannite show that each contains an asymmetrical carbon, thus: —



$$\begin{array}{c} \mathrm{COH} \\ | \\ \mathrm{HO-C-H} \\ | \\ \mathrm{CH.OH} \\ | \\ \mathrm{(CHOH)_2} \\ | \\ \mathrm{CH_2OH} \end{array}$$

**Galactose, $C_6H_{12}O_6$.** — This substance is formed together with dextrose when either sugar of milk or gum arabic is boiled with dilute sulphuric acid.

It crystallizes in large rhombic prisms, which melt at 130°; is easily soluble in hot water, but much less so in cold water; less sweet than cane sugar; turns the plane of polarization to the left; conducts itself in some respects like dextrose. It reduces Fehling's solution; gives mucic acid with nitric acid, and dulcite with sodium amalgam. It does not ferment with yeast.

### THE CANE-SUGAR GROUP, $C_{12}H_{22}O_{11}$.

**Cane sugar, $C_{12}H_{22}O_{11}$.** — This well-known variety of sugar occurs very widely distributed in nature, in sugar cane, sorghum, the Java palm, the sugar maple, beets, madder root, coffee, walnuts, hazel nuts, sweet and bitter almonds; in the blossoms of many plants; in honey, etc., etc.

It is obtained mainly from the sugar cane and from beets. In either case the processes of extraction and refining are largely mechanical. When sugar cane is used, this is macerated with water to dissolve the sugar. Thus a dark-colored solution is obtained. This is evaporated, and then passed through filters of bone-black which remove the coloring matter. The solution is evaporated in the air to some extent, and then in *large vessels* called "vacuum pans," from which the air is partly exhausted, so that the boiling takes place at a lower temperature than would be required under the ordinary pressure of the atmosphere. The mixture of crystals and mother liquors obtained from the "vacuum pans" is freed from the liquid by being brought into the "centrifugals." These are funnel-shaped sieves which are revolved very rapidly, the liquid being thus thrown by centrifugal force through the openings of the sieve, while the crystals remain behind and are thus nearly dried. The final drying is effected by placing the crystals in a warm room.

When beets are used the process is essentially the same, though there are some differences in the details.

The mother liquors which are obtained from the "centrifugals" are further evaporated, and yield lower grades of sugar; and, finally, a syrup is obtained which does not crystallize. This is *molasses*. Molasses is sometimes brought into the market as such; sometimes, particularly when obtained from beet sugar, it is allowed to ferment for the purpose of making alcohol. The spent wash, or waste liquor, "vinasse," is now evaporated to dryness and calcined for the purpose of getting the alkaline salts contained in the residues. The products of distillation are collected, and from them are separated methyl alcohol and tri-methyl-amine (see p. 96).

Sugar crystallizes from water in well-formed, large monoclinic prisms. It is dextro-rotatory. When heated to 210° to 220°, cane sugar loses water, and is converted into the substance called *caramel*, which is more or less brown in color, according to the duration of the heating and the temperature reached. Boiled with dilute acids, cane sugar is split into equal parts of dextrose and levulose, as has been stated. The mixture of the two is called *invert-sugar*. The process is called *inversion*. It takes place, to some extent, when impure sugar is allowed to stand. Hence invert-sugar is contained in the brown sugars found in the market. Yeast gradually transforms cane sugar into dextrose and levulose, and these then undergo fermentation. Cane sugar itself does not ferment.

**Experiment 39.** Arrange two pieces of apparatus as in Exp. 7. In one put $40^{g}$ to $50^{g}$ grape sugar and a certain quantity of yeast, as in Exp. 7; in the other put the same amount of cane sugar and of yeast. Notice the difference.

Cane sugar does not reduce an alkaline solution of copper sulphate.

**Experiment 40.** Prepare a dilute solution of cane sugar by dissolving $1^{g}$ to $2^{g}$ in $200^{cc}$ water. Test this with Fehling's solution, as in Exp. 38. Now add to the sugar solution 10 drops concentrated hydrochloric acid, and heat for half an hour on the water-bath at 100°; exactly neutralize the acid with a dilute solution of sodium carbonate, and test with Fehling's solution.

Oxidizing agents readily convert cane sugar into oxalic acid (see Exp. 34) and saccharic acid.

Like dextrose, cane sugar forms compounds with metals, metallic oxides, and salts. Among these the following may be mentioned: —

| | | |
|---|---|---|
| | *Sodium sucrate* . . . . | $C_{12}H_{21}O_{11}.Na$, |
| | *Sodium-chloride sucrate* . . | $C_{12}H_{22}O_{11}.NaCl$, |
| | *Calcium sucrate* . . . . | $C_{12}H_{20}O_{11}.Ca$, |
| and | *Lime sucrate* . . . . . | $C_{12}H_{22}O_{11}.2\,CaO$. |

These derivatives are not sweet.

An *oct-acetate* of the formula $C_{12}H_{14}(C_2H_3O)_8O_{11}$ has been made by treating sugar with sodium acetate and acetic anhydride.

Though cane sugar readily breaks up into dextrose and levulose, no one has succeeded as yet in effecting the union of these two substances to form cane sugar. The character of the relation between it and the two glucoses is not understood.

**Sugar of milk, lactose, $C_{12}H_{22}O_{11} + H_2O$.** — This sugar occurs in the milk of all mammals. It is obtained in the manufacture of cheese. The caseïn is separated from the milk by means of rennet. The sugar of milk remains in solution, is separated by evaporation, and purified by recrystallization. It crystallizes in rhombic crystals. That which comes into the market has been crystallized on strings or wood splinters. It has a slightly sweet taste; is much less soluble in water than cane sugar, and is dextro-rotatory. It reduces Fehling's solution. Oxidized with nitric acid, it yields mucic and saccharic acids. Nascent hydrogen converts sugar of milk into mannite, dulcite, and other substances. Like dextrose and cane sugar, it forms compounds with bases, dissolving lime, baryta, lead oxide, etc.

Sugar of milk ferments under certain circumstances, and breaks up into alcohol and lactic acid. The souring of milk is a result of this fermentation. The lactic acid formed coagulates the casein; hence the thickening.

**Maltose, $C_{12}H_{22}O_{11}$.** — This carbohydrate is formed by the action of *malt* on starch. Malt, which is made by steeping barley in water until it germinates, and then drying it, contains a substance called *diastase*, which has the power of effecting changes similar to some of those effected by the ferments. Thus, it acts upon starch, and converts it into dextrin and maltose: —

$$\underset{\text{Starch.}}{3\,C_6H_{10}O_5} + H_2O = \underset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \underset{\text{Dextrin.}}{C_6H_{10}O_5}.$$

Maltose is also formed by the action of dilute sulphuric acid upon starch, and is hence contained in commercial glucoses. By further treatment with sulphuric acid it is converted into dextrose. Maltose crystallizes in fine needles; is dextro-rotatory; reduces Fehling's solution, and ferments with yeast.

### THE CELLULOSE GROUP, $C_6H_{10}O_5$.

**Cellulose, $C_6H_{10}O_5$.** — Cellulose forms, as it were, the ground work of all vegetable tissues. It presents different appearances and different properties, according to the source from which it is obtained; but these differences are due to substances with which the cellulose is mixed; and when they are removed, the cellulose left behind is the same thing, no matter what its source may have been. The coarse wood of trees, as well as the tender shoots of the most delicate plants, all contain cellulose as an essential constituent. It forms the membrane of the cells. Cotton-wool, hemp, and flax consist almost wholly of cellulose.

For the preparation of cellulose, either Swedish filter-paper or cotton-wool may be taken.

**Experiment 41.** Treat some cotton-wool successively with ether, alcohol, water, a caustic alkali, and, finally, a dilute acid. Then wash with water.

Cellulose is amorphous; insoluble in all ordinary solvents; soluble in an ammoniacal solution of cupric oxide.

**Experiment 42.** Add some ammonium chloride to a solution of copper sulphate; precipitate with caustic soda; filter, and carefully wash. Dissolve the cupric hydroxide thus obtained in ammonia. The solution is known as *Schweizer's reagent.* It will dissolve cellulose. Try it with some of the cellulose obtained in Exp. 41.

Cellulose dissolves in concentrated sulphuric acid. If the solution be diluted and boiled, the cellulose is converted into dextrin and dextrose. It will thus be seen that rags, which consist largely of cellulose, paper, and wood, might be used for the preparation of dextrose or glucose, and consequently of alcohol.

**Gun cotton, pyroxylin, nitro-cellulose.** — Cellulose has some of the properties of alcohols; among them the power to form ethereal salts with acids. Thus, when treated with nitric acid, it forms several nitrates, just as glycerin forms the nitrates known as nitro-glycerin (which see).

Treated for a short time with sulphuric and nitric acids, *cellulose is* converted into the lower nitrates, particularly the tetra- and penta-nitrates. A solution of these in a mixture of ether and alcohol is known as *collodion solution*, which is much used in photography. When poured upon any surface, such as glass, the ether and alcohol rapidly evaporate, leaving a thin coating of the nitrates which were in solution.

When treated for twenty-four hours at 10° with a mixture of nitric and sulphuric acids, cellulose yields the *hexa-nitrate* $C_{12}H_{14}O_4(O.NO_2)_6$, which is used as an explosive under the name of gun cotton. It is used chiefly for blasting.

An intimate mixture of gun cotton and camphor has come into extensive use under the name of *celluloid*. As it is plastic at a slightly elevated temperature, it can easily be moulded into any desired shape. When it cools it hardens.

**Paper.** — Paper in its many forms consists mainly of cellulose. The essential features in the manufacture of paper are, first, the disintegration of the substances used. This is effected partly mechanically, and partly by boiling with caustic soda. Then it is converted into pulp by means of knives placed on rollers. The pulp, with the necessary quantity of water, is then passed between rollers. Chiefly rags of cotton or linen are used in the manufacture of paper; wood and straw are also used.

**Starch, $C_6H_{10}O_5$.** — Starch is found everywhere in the vegetable kingdom in large quantity, particularly in all kinds of grain, as maize, wheat, etc.; in tubers, as the potato, arrowroot, etc.; in fruits, as chestnuts, acorns, etc.

In the United States starch is manufactured mainly from maize; in Europe, from potatoes.

The processes involved in the manufacture of starch are mostly mechanical. The maize is first treated with warm water; the softened grain is then ground between stones, a stream of water running continuously into the mill. The thin paste which is carried away is brought upon sieves of silk bolting-cloth, which are kept in constant motion. The starch passes through with the water as a milky fluid. This is allowed to settle when the water is drawn off. The starch is next treated with water containing a little alkali (caustic soda, or sodium carbonate), the object of which is to dissolve gluten, oil, etc. The mixture is now brought into shallow, long wooden runs, where the starch is deposited, the alkaline water running off. Finally, the starch is washed with water, and dried at a low temperature.

Starch has a granular structure, the grains as seen under the microscope having a series of concentric markings, of which the nucleus appears to be at one side.

Starch in its usual condition is insoluble in water. If ground with cold water, it is partly dissolved. If heated with water, the membranes of the starch-cells are broken, and the contents form a partial solution. On cooling, it forms a transparent jelly called *starch paste*.

With iodine, starch paste gives a deep blue color; with bromine, a yellow color.

**Experiment 43.** Make some starch paste thus: Put a few grams of starch[1] in an evaporating dish; pour enough cold water upon it to cover it; grind it under the water with a pestle, and then pour $200^{cc}$ to $300^{cc}$ hot water upon it. When this is cool, add a few drops to a litre of water, and then add a few drops of potassium iodide. As long as the iodine is in combination with the potassium no change of color takes place; but if the iodine be set free by the addition of a drop or two of chlorine water, or of strong nitric acid, the entire liquid turns a beautiful dark blue. The cause of this color is the formation of a very unstable compound of starch and iodine. The color is easily destroyed by a slight excess of chlorine water (try it in a test-tube); by alkalies (try it); by sulphurous acid (try it); by hydrogen sulphide (try it); etc. It is also destroyed by heating. (Heat some of the solution in a test-tube, and let it stand.) The color reappears on cooling.

---

[1] The purest form of starch to be found in the market is that made from arrow-root. *Ordinary starch* contains other substances which sometimes interfere with the reactions.

**Experiment 44.** Use some of the starch paste in studying the effect of bromine upon it. Use dilute solutions. The bromine must be in the free condition.

It has been stated that starch is converted into dextrin, maltose, and dextrose by dilute acids; and that diastase converts it into maltose and dextrin.

**Experiment 45.** Add $20^{cc}$ concentrated hydrochloric acid to $200^{cc}$ of the starch paste already made, and heat for two hours on the water-bath, connecting the flask with an inverted condenser (see Fig. 8). Then examine with Fehling's solution. Test, also, some of the original starch paste with Fehling's solution.

**Dextrin, $C_6H_{10}O_5$.** — Dextrin, as has been stated, is formed by treating starch with dilute acids or diastase. It is converted by further treatment with acids into dextrose. The substance ordinarily called dextrin has been shown to be a mixture of several isomeric substances which resemble each other very closely. The mixture is an uncrystallizable solid. It is strongly dextro-rotatory; gives a red color with iodine, and does not reduce Fehling's solution. It is used extensively as a substitute for gum.

**Gums.** — Under this head are included a number of substances which occur in nature. One of the best known is *gum arabic*, which is obtained in Senegambia from the bark of trees belonging to the *Acacia* variety. Its formula, like that of cane sugar, is $C_{12}H_{22}O_{11}$. Other gums are *wood gum*, obtained from the birch, ash, beech, etc.; *bassorin*, the chief constituent of gum tragacanth, etc.

Our knowledge of the chemistry of these gums is very limited.

# CHAPTER XII.

## MIXED COMPOUNDS CONTAINING NITROGEN.

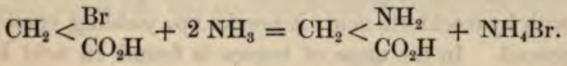
In speaking of the preparation of bibasic acids from monobasic acids, reference was made to cyan-acetic and the two cyan-propionic acids. These are nothing but simple cyanogen substitution-products analogous to chlor-acetic and the two chlor-propionic acids. They are made by treating the chlorine products with potassium cyanide. They have been useful chiefly in the preparation of bibasic acids, as described in connection with malonic and the two succinic acids. It will therefore not be necessary to consider them individually here.

Note for Student. — How may malonic be made from acetic acid; and the two succinic acids from propionic acid? Give the equations.

The chief substances to be considered under the head of *mixed compounds containing nitrogen* are the *amido-acids* and the *acid amides*. As will be seen, both these classes of substances are of special interest, as they represent forms of combination which are favorite ones in nature, especially in the animal kingdom, some of the most important substances found in the animal body, such as urea, uric acid, glycocoll, etc., belonging to one or both the classes.

### Amido-acids.

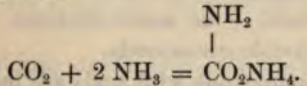
The relation of an amido-acid to the simple acid is, as the name implies, the same as that of an amido derivative of a hydrocarbon to the hydrocarbon. That is to say, it may be regarded as the acid in which a hydrogen is replaced by the *amido group*, $NH_2$. Thus, amido-acetic acid is represented by the formula $CH_2<\begin{matrix}NH_2\\CO_2H\end{matrix}$; while amido-methane, or methyl-amine is represented thus, $CH_3 . NH_2$. The reasons for regarding methyl-amine as a substituted ammonia, as represented, have been stated. The formula is based upon the reactions of the substance; that is, upon its chemical conduct and the methods used in its preparation. The same arguments might be advanced in favor of the view that the amido-acids are substituted ammonias, and, at the same time, acids. The simplest method for their preparation consists in treating halogen derivatives of the acids with ammonia; thus amido-acetic acid may be made by treating brom-acetic acid with ammonia: —



$$CH_2<\begin{matrix}Br\\CO_2H\end{matrix} + 2\,NH_3 = CH_2<\begin{matrix}NH_2\\CO_2H\end{matrix} + NH_4Br.$$

NOTE FOR STUDENT. — Compare this reaction with that made use of for making methyl-amine.

**Amido-formic acid, carbamic acid,** $\begin{matrix}NH_2\\|\\CO_2H\end{matrix}$. — This acid is not known in the free condition. Its ammonium salt, $\begin{matrix}NH_2\\|\\CO_2NH_4\end{matrix}$, is formed when carbon dioxide and ammonia are brought together: —

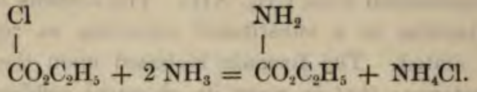


$$CO_2 + 2\,NH_3 = \begin{matrix}NH_2\\|\\CO_2NH_4.\end{matrix}$$

The other carbamates may be prepared from the ammonium salt. They are decomposed, yielding carbonates and ammonia. Thus, when potassium carbamate is warmed in water solution, decomposition takes place, as represented in the equation, —

$$NH_2.CO_2K + H_2O = NH_3 + HKCO_3.$$

The *ethereal salts* of carbamic acid are readily made by treating the ethereal salts of chlor-formic acid (see p. 157) with ammonia: —



$$\begin{array}{l}\mathrm{Cl}\\ |\\ \mathrm{CO_2C_2H_5}\end{array} + 2\,\mathrm{NH_3} = \begin{array}{l}\mathrm{NH_2}\\ |\\ \mathrm{CO_2C_2H_5}\end{array} + \mathrm{NH_4Cl}.$$

Amido-formic acid cannot be taken as a fair representative of the amido-acids, any more than carbonic acid can be taken as a fair representative of the hydroxy-acids.

**Glycocoll, glycine, amido-acetic acid,** $\left.\right\}$ $C_2H_5NO_2\left(= CH_2 < \begin{array}{l}NH_2\\ CO_2H\end{array}\right)$. — In the bile are contained two complicated acids, which are known as glycocholic and taurocholic acids. When glycocholic acid is boiled with hydrochloric acid, it breaks up, yielding cholic acid and glycocoll. In the urine of horses is found an acid known as hippuric acid. When this is boiled with hydrochloric acid, it breaks up into benzoic acid and glycocoll.

When uric acid is treated with hydriodic acid, glycocoll is one of the products. Further, glycocoll is formed when glue is boiled with baryta water or dilute sulphuric acid. Its formation from brom-acetic acid and ammonia, mentioned above, gives the clearest indication in regard to its relation to acetic acid.

Amido-acetic acid has both acid and basic properties. It unites with acids, forming weak salts; and it acts upon bases, giving salts with metals, — the amido-acetates. It also unites with salts, forming double compounds.

Examples of the compounds with acids are the

*Hydrochloride* . . . . $CH_2 < \begin{array}{l}NH_2 . HCl\\ CO_2H\end{array}$,

and the *Nitrate* . . . . . . . $CH_2 < \begin{array}{l}NH_2 . HNO_3\\ CO_2H\end{array}$;

of the salts with metals,

*Zinc amido-acetate* . $Zn(C_2H_4NO_2)_2 + H_2O$,

*and* *Copper amido-acetate* . $Cu(C_2H_4NO_2)_2 + H_2O$;

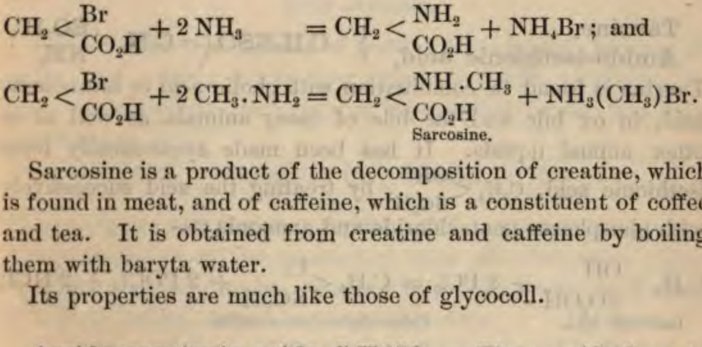
of the compounds with salts, the double salt of

$$\left.\begin{array}{l}\quad\textit{Copper nitrate}\\ \text{and }\textit{Copper amido-acetate,}\end{array}\right\}\mathrm{Cu(NO_3)_2.Cu(C_2H_4NO_2)_2 + 2\,H_2O}.$$

Treated with nitrous acid, glycocoll is converted into hydroxy-acetic acid.

Note for Student. — Write the equation representing the reaction which takes place when glycocoll is treated with nitrous acid.

**Sarcosine, methyl-glycocoll, $C_3H_7NO_2\left(=CH_2<\begin{matrix}NH.CH_3\\ CO_2H\end{matrix}\right)$.** If brom-acetic acid be treated with methyl-amine instead of with ammonia, a reaction takes place similar to that which takes place with ammonia, the product being *methyl glycocoll* or *sarcosine*: —



$$CH_2<\begin{matrix}Br\\ CO_2H\end{matrix} + 2\,NH_3 = CH_2<\begin{matrix}NH_2\\ CO_2H\end{matrix} + NH_4Br\text{; and}$$

$$CH_2<\begin{matrix}Br\\ CO_2H\end{matrix} + 2\,CH_3.NH_2 = \underset{\text{Sarcosine.}}{CH_2<\begin{matrix}NH.CH_3\\ CO_2H\end{matrix}} + NH_3(CH_3)Br.$$

Sarcosine is a product of the decomposition of creatine, which is found in meat, and of caffeine, which is a constituent of coffee and tea. It is obtained from creatine and caffeine by boiling them with baryta water.

Its properties are much like those of glycocoll.

**Amido-propionic acids, $C_3H_7NO_2$.** — These acids bear to propionic acid relations similar to that which amido-acetic acid bears to acetic acid. There are two, corresponding to α- and β-chlor-propionic acids, from which they are made. They are not found in nature. Their properties are much like those of glycocoll.

Note for Student. — What substances would be formed by treating the two amido-propionic acids with nitrous acids?

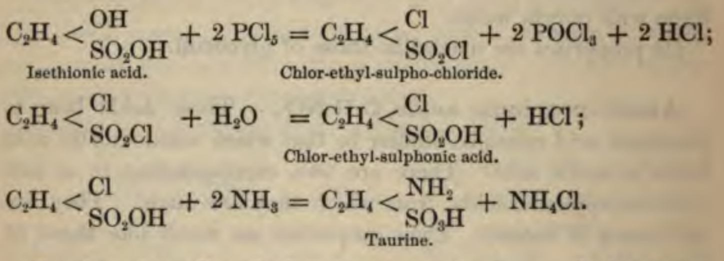
Among the amido derivatives of the higher members of the fatty acid series, that of caproic acid should be specially mentioned.

**Leucine, α-amido-caproic acid,**
**$C_6H_{13}NO_2$ [$=CH_3.CH_2.CH_2.CH_2.CH(NH_2).CO_2H$].**
Leucine is found very widely distributed in the animal kingdom, as in the spleen, pancreas, and brain. It has also been found in the vegetable kingdom in a few plants. It is produced by the decomposition of substances containing albumin or gelatin. It has been made by treating α-brom-caproic acid with ammonia.

### AMIDO-SULPHONIC ACIDS.

Just as there are amido derivatives of the carbonic acids, so, too, there may be amido derivatives of the sulphonic acids. Only one of these need be considered.

**Taurine, Amido-isethionic acid,** $\left.\right\}$ **$C_2H_7NSO_3\left(=C_2H_4<\substack{SO_3H\\NH_2}\right)$.**
Taurine is found in combination with cholic acid in taurocholic acid, in ox bile and the bile of many animals, as well as in other animal liquids. It has been made synthetically from isethionic acid, $C_2H_4<\substack{OH\\SO_3H}$, by treating the acid successively with phosphorus pentachloride and ammonia:—



$$C_2H_4<\substack{OH\\SO_2OH}+2\,PCl_5=C_2H_4<\substack{Cl\\SO_2Cl}+2\,POCl_3+2\,HCl;$$

Isethionic acid. Chlor-ethyl-sulpho-chloride.

$$C_2H_4<\substack{Cl\\SO_2Cl}+H_2O=C_2H_4<\substack{Cl\\SO_2OH}+HCl;$$

Chlor-ethyl-sulphonic acid.

$$C_2H_4<\substack{Cl\\SO_2OH}+2\,NH_3=C_2H_4<\substack{NH_2\\SO_3H}+NH_4Cl.$$

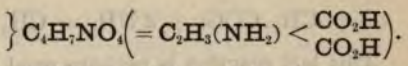
Taurine.

Taurine crystallizes in large tetragonal prisms. It is a very stable substance, and can be boiled with concentrated acids without decomposition. With nitrous acids it yields isethionic acid.

It unites with bases forming salts.

The only amido-bibasic acid which need be considered is amido-succinic acid.

**Aspartic acid,**
**Amido-succinic acid,**



$$\left.\begin{array}{l}\text{Aspartic acid,}\\ \text{Amido-succinic acid,}\end{array}\right\} C_4H_7NO_4\left(=C_2H_3(NH_2)<\begin{array}{l}CO_2H\\ CO_2H\end{array}\right).$$

Aspartic acid occurs in pumpkin seeds, and is frequently met with as a product of boiling various natural compounds with dilute acids. Thus, for example, it is formed when caseïn and albumin are treated in this way. It is formed also when asparagine (which see) is boiled with acids or alkalies.

Aspartic acid crystallizes. It turns the plane of polarization, under some circumstances to the right, under others to the left.

Treated with nitrous acids it yields malic acid.

## ACID AMIDES.

When the ammonium salt of acetic acid is heated, it gives off water, and a body distils over which is known as *acetamide*. The reaction which takes place is represented by the following equation: —

$$CH_3.COONH_4 = CH_3.CONH_2 + H_2O.$$

The substance obtained has neither acid nor basic properties. An examination of the ammonium salts of other acids shows that the reaction is a general one, and we thus may get a class of neutral bodies, known as the *acid amides*.

As no one of the acid amides of the fatty acid series is of special importance, a few words of a general character in regard to the class will suffice.

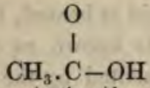
Besides the reaction above referred to for making the acid amides, there are two others of general application. One consists in treating an ethereal salt of an acid with ammonia; thus, when ethyl acetate is treated with ammonia, this reaction takes place: —

$$CH_3.CO_2C_2H_5 + NH_3 = CH_3.CONH_2 + C_2H_6O.$$

The other reaction consists in treating the acid chlorides with ammonia. Thus, to get acetamide, we may treat acetyl chloride (see p. 61) with ammonia: —

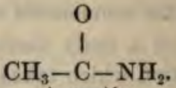
$$CH_3.COCl + 2\,NH_3 = CH_3.CONH_2 + NH_4Cl.$$

This last reaction is perhaps used most frequently. It shows the relation which exists between acetic acid and acetamide. For acetyl chloride is made from acetic acid by treatment with phosphorus trichloride, and is, therefore, as has been pointed out, to be regarded as acetic acid in which the hydroxyl is replaced by chlorine. Now, by treatment with ammonia the same reaction takes place as that which we have had to deal with in the preparation of amido-acids, the chlorine is replaced by the amido group. Therefore, acetamide is acetic acid in which the hydroxyl is replaced by the amido group, as shown in the formulas: —



$$CH_3.\overset{\overset{O}{|}}{C}-OH$$

Acetic acid.



$$CH_3-\overset{\overset{O}{|}}{C}-NH_2.$$

Acetamide.

As the acid hydrogen of the acid is replaced, the amide is not an acid. On the other hand, the basic properties of the ammonia are destroyed by the presence of the acid residue as a part of its composition. This latter fact may be stated in another way; viz., when an ammonia residue is in combination with carbon, which in turn is in combination with oxygen, its basic properties are destroyed.

The amides are converted into ammonia and a salt when boiled with strong bases: —

$$CH_3.CONH_2 + KOH = CH_3CO_2K + NH_3.$$

They are converted into cyanides by treatment with phosphorus pentoxide $P_2O_5$: —

$$CH_3.CONH_2 = CH_3.CN + H_2O.$$

As the substance obtained in this way is identical with methyl cyanide, which is formed by treating methyl-sulphuric acid with potassium cyanide, the reaction furnishes additional evidence in favor of the conclusion already reached; viz., that in the cyanides the carbon and not the nitrogen of the cyanogen group is in combination with the hydrocarbon residue, as represented in the formula $CH_3-C-N$.

As acetamide is made by treating ammonia with the chloride of acetic acid, so, by treating ammonia with the chloride of any acid, the corresponding amide may be made. So, also, by treating ammonia with acid chlorides, or by treating acid amides with strong acids, more complicated compounds may be obtained. Of these *di-acetamide*, $NH\begin{cases} C_2H_3O \\ C_2H_3O \end{cases}$, and *tri-acetamide*, $N\begin{cases} C_2H_3O \\ C_2H_3O, \\ C_2H_3O \end{cases}$ may serve as examples. The relations of these substances to ammonia and to acetic acid are shown by the formulas, ordinary or mon-acetamide being $NH_2.C_2H_3O$ or $CH_3.CO.NH_2$.

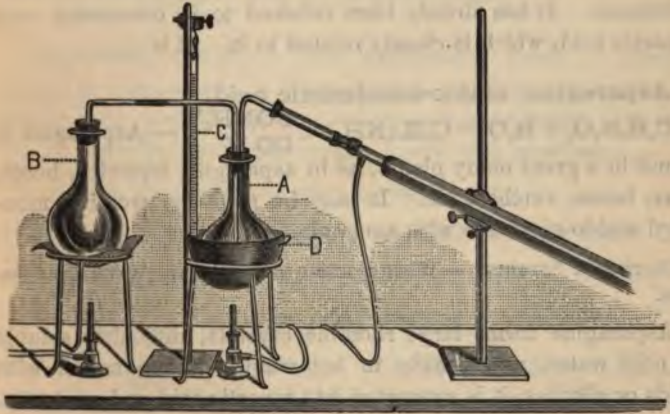
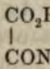
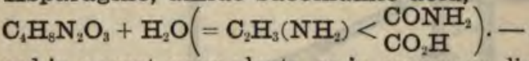


Fig. 12.

**Experiment 46.** Arrange an apparatus as shown in Fig. 12. In flask *A* put 150g oxalic acid (dehydrated at 100°) and 100g absolute alcohol; and, in flask *B*, 100g absolute alcohol. Heat the bath *D* to 100°; and then heat the alcohol in flask *B* to boiling, and continue to pass the vapor from flask *B* into the mixture in flask *A*, meanwhile allowing the temperature of the oil-bath to rise to 125°–130°. A mixture of alcohol and ethyl oxalate will distil over. To some of this mixture in a flask add concentrated aqueous ammonia, and shake. Insoluble oxamide is formed and is thrown down as a white powder. What reactions have taken place? Write the equations. Filter off the oxamide, and wash it with water. See whether it conducts itself like an acid. Has it an acid reaction? Boil with caustic potash (not too much), and notice whether ammonia is given off. Why does it dissolve? How can the oxalic acid be extracted from the solution?

When the amide of a poly-basic acid is boiled with ammonia, and under some other circumstances, partial decomposition takes place, and a substance is formed which is both amide and acid. Thus, in the case of oxamide, the product is *oxamic acid*,  $\begin{array}{l}CO_2H\\ |\\ CONH_2\end{array}$. This acid forms well-characterized salts and other derivatives, such as are obtained from acids in general. There is one acid of this kind which is a well-known natural substance. It has already been referred to in connection with aspartic acid, which is closely related to it. It is

**Asparagine, amido-succinamic acid,**
 $C_4H_8N_2O_3 + H_2O\left(= C_2H_3(NH_2) < \begin{array}{l}CONH_2\\ CO_2H\end{array}\right)$. — Asparagine is found in a great many plants, as in asparagus, liquorice, beets, peas, beans, vetches, etc. It may be made by treating monethyl amido-succinate with ammonia.

Note for Student. — What reaction takes place? Write the equation.

Asparagine forms large rhombic crystals, difficultly soluble in cold water, more easily in hot water. When boiled with acids or alkalies, it is converted into aspartic acid and ammonia.

Note for Student. — Notice that only the amido group of the amide is driven out of the compound by this treatment. The other amido group which is contained in the hydrocarbon portion of the compound is not disturbed.

Nitrous acid converts asparagine into malic acid.

**Cyan-amides, $CN_2H_2$.**— In speaking of cyanic acid, the existence of two chlorides of cyanogen was mentioned: one a liquid, having the formula CNCl; the other a solid, of the formula $C_3N_3Cl_3$. When the former is treated with ammonia, it is converted into an amide, $CN.NH_2$, which bears to cyanic acid, NC.OH, the relation of an amide. Like the other simple compounds of cyanogen, cyan-amide readily undergoes change. When simply kept unmolested, it is converted into *di-cyan-diamide*, $C_2N_4H_4$; while, when heated to 150°, a violent reaction takes place, and *tri-cyan-triamide*, $C_3N_6H_6$, is formed. Whether or not the formulas given really express the true molecular weights of the products is not known. It can only be said that the changes involve no change in per centage composition, and therefore are cases of polymerisation. The formation of the compounds is particularly interesting, as illustrating the tendency on the part of the simpler cyanides to undergo change under very slight provocation.

**Guanidine, $CN_3H_5$.** — This substance, which is closely related to cyan-amide, is formed by the oxidation of guanine (which see), and this in turn is obtained from guano. It may also be made by treating cyanogen iodide with ammonia: —

$$CNI + 2\,NH_3 = CN_3H_5.HI,$$

the product being the hydriodic-acid salt of guanidine. As will be seen, guanidine is cyan-amide plus ammonia: —

$$CN.NH_2 + NH_3 = CN_3H_5.$$

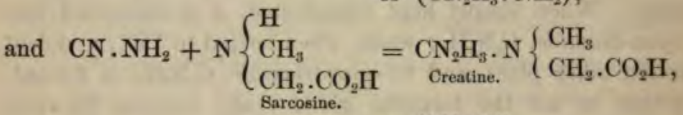
It is a strongly alkaline base. Boiled with dilute sulphuric acid or baryta water, it yields urea and ammonia: —

$$\underset{\text{Guanidine.}}{CN_3H_5} + H_2O = \underset{\text{Urea.}}{CON_2H_4} + NH_3.$$

**Creatine, $C_4H_9N_3O_2$.** — This substance is found in the muscles of all animals. It is closely related to guanidine and also to sarcosine (see p. 193). It has been made synthetically by bringing cyan-amide and sarcosine together. The reaction which takes place is analogous to that made use of for the preparation of guanidine. The analogy is shown by the two equations, —

$$CN.NH_2 + NH_3 = \underset{\text{Guanidine.}}{CN_3H_5},$$

$$\text{or } (CN_2H_3.NH_2),$$



$$\text{and } CN.NH_2 + \underset{\text{Sarcosine.}}{N\left\{\begin{matrix}H\\CH_3\\CH_2.CO_2H\end{matrix}\right.} = \underset{\text{Creatine.}}{CN_2H_3.N\left\{\begin{matrix}CH_3\\CH_2.CO_2H\end{matrix}\right.},$$

$$\text{or } C_4H_9N_3O_2.$$

**Urea, or carbamide and derivatives.** — Closely related to the nitrogen compounds just considered is urea, or the amide of carbonic acid. Its importance and certain peculiarities distinguish it from the other acid amides, and it is therefore considered by itself.

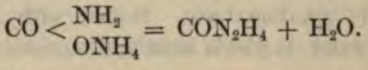
Urea is found in the urine and blood of all mammals, and particularly in the urine of carnivorous animals. Human urine contains from 2 to 3 per cent; the quantity given off by an adult man in 24 hours being about $30^g$. Urea may be made by the following methods: —

(1) By treating carbonyl chloride with ammonia: —

$$COCl_2 + 2\,NH_3 = CON_2H_4 + 2\,HCl.$$

What is the analogous reaction for the preparation of acetamide?

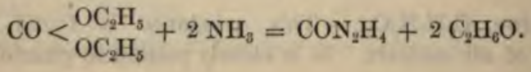
(2) By heating ammonium carbamate: —



$$CO<^{NH_2}_{ONH_4} = CON_2H_4 + H_2O.$$

What is the analogous reaction for preparing oxamide?

(3) By treating ethyl carbonate with ammonia: —



$$CO<^{OC_2H_5}_{OC_2H_5} + 2\,NH_3 = CON_2H_4 + 2\,C_2H_6O.$$

(4) By the addition of water to cyan-amide: —

$$CN.NH_2 + H_2O = CON_2H_4.$$

(5) By evaporation of ammonium cyanate in aqueous solution: —

$$CN(ONH_4) = CON_2H_4.$$

This reaction is of special interest, for the reason that it afforded the first example of the formation, by artificial methods from inorganic substances, of an organic compound found in the animal body (see p. 1).

Urea is most readily obtained from urine.

**Experiment 47.** Evaporate four or five litres *fresh* urine to a thin, syrupy consistence. After cooling add ordinary concentrated nitric acid, when crystals of urea nitrate are obtained. Filter, wash, and recrystallize from moderately concentrated nitric acid. When the crystals of urea nitrate are white, dissolve again in water, and add finely-powdered barium carbonate. The nitric acid forms barium nitrate, and the urea is left in free condition. Evaporate to dryness, and from the residue extract the urea with strong alcohol.

**Experiment 48.** Make potassium cyanate as directed in Experiments 24, p. 82, and 26, p. 83. To the cold solution of the cyanate add a solution of ammonium sulphate containing as much of the salt as there was used of potassium ferrocyanide in the preparation of the cyanate. Evaporate to a small volume, and allow to cool. Potassium sulphate will crystallize out. Filter this off, and evaporate to dryness. Extract with alcohol. The urea will crystallize from the alcoholic solution when it is brought to the proper concentration. Give all the reactions involved in passing from potassium ferrocyanide to urea. Compare the urea made artificially with that made from urine.

Urea crystallizes from alcohol in large quadratic prisms, which melt at 132°.

**Experiment 49.** Determine the melting-points of both the natural and artificial specimens of urea.

Urea is easily soluble in water and alcohol. Heated with water in a sealed tube to 100°, it breaks up into carbon dioxide and ammonia: —

$$CON_2H_4 + H_2O = CO_2 + 2\,NH_3.$$

The same decomposition of the urea takes place spontaneously when urine is allowed to stand. Hence the odor of ammonia is always noticed in the neighborhood of urinals which are not kept thoroughly clean.

Sodium hypochlorite or hypobromite decomposes urea into carbon dioxide, nitrogen, and water: —

$$CON_2H_4 + 3\,NaOCl = Na_2CO_3 + NaCl + N_2 + H_2O + 2\,HCl.$$

**Experiment 50.** To a solution of 20$^g$ sodium hydroxide in 100$^{cc}$ water add about 5$^{cc}$ bromine, and shake well. Make a solution of urea in water, and add to the solution of the hypobromite. An evolution of gas will be noticed, showing that the urea is decomposed.

Nitrous acid acts in the same way: —

$$CON_2H_4 + 2\,HNO_2 = CO_2 + N_4 + 3\,H_2O.$$

When heated, urea loses ammonia, and yields first ***biuret***, and finally *cyanuric acid* (see p. 84): —

$$2\,CO(NH_2)_2 = \underset{\text{Biuret.}}{C_2H_5N_3O_2} + NH_3;$$

$$3\,CO(NH_2)_2 = \underset{\text{Cyanuric acid.}}{C_3H_3O_3N_3} + 3\,NH_3.$$

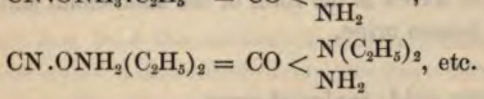
Urea unites with acids, bases, and salts. The hydrogen of the amido groups may be replaced by acid or alcohol radicals, giving compounds of which *acetyl urea*, $CO<\begin{matrix}NH.C_2H_3O\\NH_2\end{matrix}$, and *ethyl urea*, $CO<\begin{matrix}NHC_2H_5\\NH_2\end{matrix}$, are examples.

Among the compounds with acids, the following may be mentioned: *urea hydrochloride*, $CH_4N_2O.HCl$; *urea nitrate*, $CH_4N_2O.HNO_3$; and *urea phosphate*, $CH_4N_2O.H_3PO_4$. With metals it forms such compounds as that with *mercuric oxide*, $HgO.CH_4N_2O$; with silver, $CH_2N_2O.Ag_2$, etc. With salts it forms *such compounds* as $HgCl_2.C_2H_4N_2O$, $HgO.CH_4N_2O.HNO_3$, etc.

**Substituted ureas,** — that is, those derivatives of urea which contain hydrocarbon residues in place of one or all the hydrogen atoms, — may be made from the cyanates of substituted ammonias. The fundamental reaction is the spontaneous transformation of ammonium cyanate into urea: —

$$CN.ONH_4 = CO(NH_2)_2.$$

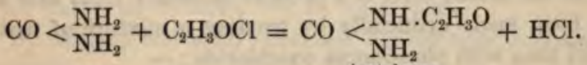
In the same way, cyanates of substituted ammonias are transformed into substituted ureas: —



$$CN.ONH_3.C_2H_5 = CO < \begin{matrix} NHC_2H_5 \\ NH_2 \end{matrix};$$

$$CN.ONH_2(C_2H_5)_2 = CO < \begin{matrix} N(C_2H_5)_2 \\ NH_2 \end{matrix}, \text{ etc.}$$

The urea derivatives which contain acid radicals are made by treating urea with the acid chlorides: —

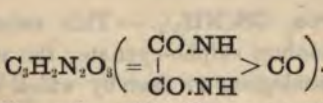


$$CO < \begin{matrix} NH_2 \\ NH_2 \end{matrix} + C_2H_3OCl = CO < \begin{matrix} NH.C_2H_3O \\ NH_2 \end{matrix} + HCl.$$

Acetyl urea.

Note for Student. — In what sense is acetyl urea analogous to acetamide?

There are several derivatives of urea and radicals of bibasic acids, as oxalic and malonic acids, which are of special interest, as they are closely related to uric acid; and their formation from this acid has thrown much needed light upon the inner nature of the acid.

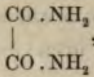


**Parabanic acid,** } $C_3H_2N_2O_3\left(= \begin{matrix} CO.NH \\ | \\ CO.NH \end{matrix} > CO\right)$. — Parabanic
**Oxalyl urea,**

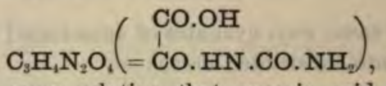
acid is formed by boiling uric acid with strong nitric acid and other oxidizing agents, and by treating a mixture of urea and oxalic acid with phosphorus trichloride: —

$$C_2H_2O_4 + CO(NH_2)_2 = C_3H_2N_2O_3 + 2\,H_2O.$$

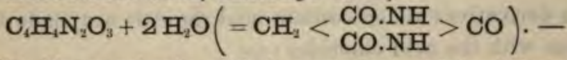
It acts like an acid. Its salts readily pass over into salts of oxaluric acid (which see). Treated with alkalies it breaks up into urea and oxalic acid. As will be seen, parabanic acid is analogous to oxamide, $\begin{array}{l}CO.NH_2\\ |\\ CO.NH_2\end{array}$, the residue of urea acting the part of the two amido groups.

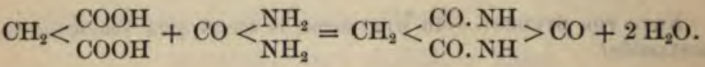


**Oxaluric acid,** $C_3H_4N_2O_4\left(= \begin{array}{l}CO.OH\\ |\\ CO.HN.CO.NH_2\end{array}\right)$, bears to parabanic acid the same relation that oxamic acid bears to oxamide. It occurs in the form of the ammonium salt in small quantity in human urine.



**Barbituric acid, malonyl urea,**
$C_4H_4N_2O_3 + 2\,H_2O\left(= CH_2 < \begin{matrix}CO.NH\\ CO.NH\end{matrix} > CO\right)$. — Barbituric acid, like parabanic acid, is a product obtained from uric acid. It has been made artificially by treating a mixture of malonic acid and urea with phosphorus oxichloride: —





$$CH_2 < \begin{matrix}COOH\\ COOH\end{matrix} + CO < \begin{matrix}NH_2\\ NH_2\end{matrix} = CH_2 < \begin{matrix}CO.NH\\ CO.NH\end{matrix} > CO + 2\,H_2O.$$

Treated with an alkali, barbituric acid breaks up into malonic acid and urea.

The relation of the acid to malonic acid and urea is the same as that of parabanic acid to oxalic acid and urea.

**Sulpho urea,** $CS(NH_2)_2$. — This substance is formed by heating ammonium sulpho-cyanate, the reaction which takes place being analogous to that by which urea is formed from ammonium cyanate: —

$$CNSNH_4 = CS(NH_2)_2.$$

A number of derivatives of sulpho urea have been made. They resemble those obtained from urea.

**Uric acid, $C_5H_4N_4O_3$.** — Uric acid occurs in human urine, in certain urinary calculi, in the urine of carnivorous animals, and of birds. The excrement of serpents consists almost entirely of ammonium urate. It has been made by heating together amido-acetic acid and urea.

Uric acid is best prepared either from serpents' excrement or guano.

It forms a crystalline powder, which is almost insoluble in water. It is a monobasic acid, though weak compounds with the alkali metals may be made which contain two atoms of metal in the molecule.

Uric acid has been the subject of a large number of interesting investigations, and many derivatives have been obtained from it. It would only tend to confusion to give an account of many of these derivatives here. Hence only a few of the transformations which have been effected, and which give an insight into the nature of the acid, will be mentioned.

1. By heating uric acid, ammonia, hydrocyanic acid and urea are formed.

2. Heated with hydriodic acid, it yields carbon dioxide, ammonia, and glycine: —

$$C_5H_4N_4O_3 + 5\,H_2O = 3\,CO_2 + 3\,NH_3 + C_2H_5NO_2.$$

3. Oxidizing agents convert uric acid either into *allantoïn*, a complicated substance of the formula $C_4H_6N_4O_3$, or *alloxan*, $C_4H_2N_2O_4$, which is closely related to parabanic acid, or oxalyl urea (see p. 203), and barbituric acid, or malonyl urea (see p. 204).

**Xanthine, $C_5H_4N_4O_2$,** is found in some rare urinary calculi and in several animal liquids. It is formed by the action of nitrous acid on guanine, $C_5H_5N_5O$: —

$$C_5H_5N_5O + HNO_2 = C_5H_4N_4O_2 + H_2O + N_2.$$

This reaction shows that guanine is an amido derivative, and that xanthine is the corresponding hydroxyl compound. (Why does this follow?)

$\left.\begin{array}{l}\textbf{Theobromine,}\\ \textbf{Dimethyl-xanthine,}\end{array}\right\}$ $C_7H_8N_4O_2[=C_5H_2(CH_3)_2N_4O_2]$, is a substance found in chocolate prepared from the seed of the cacao tree. It has been made by treating the lead compound of xanthine with methyl iodide.

**Caffeine, theine, trimethyl-xanthine,**
$C_8H_{10}N_4O_2 + H_2O\ [=C_5H\ (CH_3)_3N_4O_2 + H_2O]$, is the active constituent of coffee and tea. It has been made from theobromine by the introduction of a third methyl group.

Thus, as will be seen, a close connection is established between the active constituents of coffee, tea, and chocolate on the one hand, and xanthine and guanine on the other.

**Guanine,** $C_5H_5N_5O[=C_5H_3(NH_2)N_4O]$, is found principally in guano, from which it is prepared. Nitrous acid converts it into xanthine. Oxidizing agents convert it into guanidine, $CN_3H_5$ (see p. 199).

## Retrospect.

Before passing on to the next division of our subject, it will be well to pause and consider briefly what we have learned thus far.

In the first place, all the compounds which we have considered may be regarded as derived from the marsh-gas hydrocarbons or paraffins.

By replacing the hydrogen atoms of these hydrocarbons with chlorine, bromine, or iodine, we get (1) *the substitution-products of the hydrocarbons.*

By introducing hydroxyl into a hydrocarbon in place of hydrogen, we get the bodies called (2) *alcohols*, of which there are three classes: (*a*) the *primary*, (*b*) the *secondary*, and (*c*) the *tertiary alcohols*.

By oxidizing primary alcohols we get (3) *aldehydes*.

By oxidizing secondary alcohols we get (4) *ketones*.

By oxidizing alcohols, aldehydes, and ketones, we get (5) *acids*.

Acids and alcohols act upon each other, forming (6) *ethereal salts*, and alcohols can be converted into (7) *ethers*.

Corresponding to the oxygen derivatives, we met with compounds containing sulphur, as (8) the *sulphur alcohols*, or *mercaptans;* (9) the *sulphur ethers;* and (10) the *sulphonic acids*.

Next, we found compounds containing nitrogen. Under this head we considered *cyanogen*, and the allied compounds *hydrocyanic*, *cyanic*, and *sulpho-cyanic acids*. Allied to these we found (11) the *cyanides*, and (12) the *isocyanides;* (13) the *cyanates*, and (14) the *isocyanates;* (15) the *sulpho-cyanates*, and (16) the *iso-sulpho-cyanates* or *mustard oils*.

Finally, we found (17) *compounds containing metals in combination with radicals*.

Representatives of these various classes of compounds were considered, and the relations between them pointed out.

We found *poly-acid alcohols* and *poly-basic acids*.

Under the head of *mixed compounds* were found compounds which belong at the same time to two or more of the fundamental classes, as the *hydroxy-acids*, the *carbo-hydrates*, and the *amido-acids*. A consideration of the amido-acids and the acid amides brought us naturally to the consideration of urea and its derivatives, and of uric acid and its derivatives.

We turn now to a new class of compounds, known as *unsaturated compounds*.

## CHAPTER XIII.

## UNSATURATED CARBON COMPOUNDS. — DISTINCTION BETWEEN SATURATED AND UNSATURATED COMPOUNDS.

ALL the compounds thus far considered are generally called *saturated compounds*. This is certainly an appropriate name as far as the hydrocarbons themselves and some of the classes of their derivatives are concerned. The expression "saturated" is intended to signify that the compounds have no power to unite directly with other compounds or elements. Thus marsh gas cannot be made to unite directly with anything. Bromine, for example, must first displace hydrogen before it can enter into combination with the compound

$$CH_4 + Br_2 = CH_3Br + HBr.$$

The compound is saturated.

On the other hand, a compound which can take up elements or other compounds directly is called *unsaturated*. Thus, phosphorus trichloride is unsaturated, for it has the power to take up two chlorine atoms thus: —

$$PCl_3 + Cl_2 = PCl_5.$$

Ammonia is unsaturated, for it can take up other elements: —

$$NH_3 + HCl = NH_4Cl.$$

The condition of unsaturation is met with among carbon compounds in several forms: —

*First.* The aldehydes act like unsaturated compounds, as shown in their power to take up ammonia, hydrocyanic acid, and other substances.

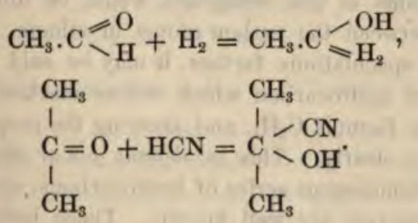
*Second.* The ketones also act like unsaturated compounds, though their power in this way is less marked than that of the aldehydes.

*Third.* The substituted ammonias are unsaturated, in the same sense in which ammonia itself is unsaturated.

*Fourth.* The cyanides take up hydrogen directly, and are therefore unsaturated also.

In the substituted ammonias, and probably in the cyanides, the unsaturation is due to the same cause as that in ammonia. In them the nitrogen is trivalent. In contact with certain substances it becomes quinquivalent, and saturates itself.

In the aldehydes and ketones, carbon is in combination with oxygen in the carbonyl condition. When they unite with hydrogen and some compounds, such as hydrocyanic acid, the relation between the carbon and oxygen is probably changed, the latter being in the hydroxyl condition. The changes are usually represented by formulas such as the following: —

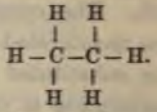


$$CH_3.C\begin{array}{l}\diagup O\\ \diagdown H\end{array} + H_2 = CH_3.C\begin{array}{l}\diagup OH\\ \diagdown H_2\end{array},$$

$$\begin{array}{c}CH_3\\ |\\ C=O\\ |\\ CH_3\end{array} + HCN = \begin{array}{c}CH_3\\ |\\ C\begin{array}{l}\diagup CN\\ \diagdown OH\end{array}\\ |\\ CH_3\end{array}.$$

In the carbonyl group the oxygen is represented as held by two bonds by the carbon atom, while in the hydroxyl condition it is represented as held by one bond. The signs may be used if care is taken to avoid a too literal interpretation of them. There are undoubtedly two relations which carbon and oxygen bear to each other in carbon compounds. These relations may be called *the hydroxyl relation*, represented by the sign C—O—, and *the carbonyl relation*, represented by the sign C = O.

*Fifth.* There is a fifth kind of unsaturation, *dependent upon differences in the relations between carbon atoms*, and it is this kind which is ordinarily meant when *unsaturated carbon compounds* are spoken of.

The kind of relation between the carbon atoms in all the saturated hydrocarbons is, so far as we know, the same as that which exists between the two carbon atoms of ethane, and which is represented by the formula  $\mathrm{H}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$. This formula signifies simply that the two carbon atoms are held together by the forces which in marsh gas enabled each carbon atom to hold one hydrogen atom. Abstracting *one hydrogen atom* from marsh gas, union is effected between the carbon atoms. What would result if *two hydrogen atoms* were to be abstracted, and union between the carbons then effected? Theoretically we should get a compound made up of two groups $CH_2$, thus $CH_2.CH_2$, and presumably the relation between the carbon atoms in this compound would be different from the relation between the carbon atoms in ethane. Without pushing these speculations farther, it may be said that there is a well-known hydrocarbon which differs markedly from ethane, having the formula $C_2H_4$, and showing the property of unsaturation very clearly. This is *olefiant gas* or *ethylene*. It is the first of a homologous series of hydrocarbons, only a very few of which, however, are well known. These hydrocarbons yield derivatives like the paraffins; though of these, as well as of the hydrocarbons, very few are known as compared with the number of the paraffin derivatives. Only a few of them are of much importance.

## ETHYLENE AND ITS DERIVATIVES.

### HYDROCARBONS, $C_nH_{2n}$.

The principal hydrocarbons of this series are included in the subjoined table: —

| | |
|---|---|
| Ethylene | $C_2H_4$. |
| Propylene | $C_3H_6$. |
| Butylene | $C_4H_8$. |
| Amylene | $C_5H_{10}$. |
| Hexylene | $C_6H_{12}$. |
| Heptylene | $C_7H_{14}$. |

The members are homologous with ethylene. They bear to the paraffins a very simple relation, each one containing two atoms of hydrogen less than the paraffin with the same number of carbon atoms.

**Ethylene, olefiant gas, $C_2H_4(=CH_2.CH_2)$.** — This gas is formed when many organic substances are subjected to dry distillation. The two principal reactions which yield it are: —

(1) The action of an alcoholic solution of potassium hydroxide on ethyl chloride, bromide, or iodide: —

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O.$$

This is the most important reaction for the preparation of the unsaturated compounds of the ethylene series. It is applicable not only to the hydrocarbons but to bodies belonging to other classes. By means of it we have it in our power to pass from any saturated compound to the corresponding unsaturated compound of the ethylene series. Thus we pass from ethane, $C_2H_6$, to ethylene, $C_2H_4$, by first introducing bromine, and then abstracting hydrobromic acid from the mono-bromine substitution-product. Similarly, by treatment with alcoholic potash of the mono-bromine substitution-products of other compounds, the corresponding unsaturated compounds may be made.

(2) The action of sulphuric acid and other dehydration agents upon alcohol: —

$$C_2H_5.OH = C_2H_4 + H_2O.$$

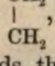
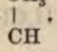
**Experiment 51.** In a flask of $2^l$ to $3^l$ capacity put a mixture of $25^g$ alcohol and $150^g$ ordinary concentrated sulphuric acid. Heat to 160° to 170°, and add gradually through a funnel tube about $500^{cc}$ of a mixture of 1 part of alcohol and 2 parts of concentrated sulphuric acid. Pass the gas through three wash bottles containing, in order, sulphuric acid, caustic soda, and sulphuric acid. Then pass it into bromine contained in a cylinder, provided with a cork with two holes. If the cylinder has a diameter of about $5^{cm}$, let the layer of bromine be about $5^{cm}$ to $7^{cm}$ thick. Upon it pour a somewhat thicker layer of water. Place the cylinder in a vessel containing cold water. Pass the gas into the bromine until it is completely decolorized.

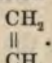
Ethylene is a colorless gas which may be condensed to a liquid. It burns with a luminous flame. With oxygen it forms an explosive mixture. *Its most characteristic property is its power to unite directly with other substances, particularly with the halogens and their hydrogen acids.* Thus it unites with chlorine and bromine, and with hydriodic and hydrobromic acids: —

$$\begin{aligned} C_2H_4 + Cl_2 &= C_2H_4Cl_2; \\ C_2H_4 + Br_2 &= C_2H_4Br_2; \\ C_2H_4 + HBr &= C_2H_5Br; \\ C_2H_4 + HI &= C_2H_5I. \end{aligned}$$

The products formed with chlorine and bromine are called *ethylene chloride* and *ethylene bromide.* They have been mentioned under the head of halogen derivatives of the paraffins. They are isomeric with *ethylidene chloride* and *ethylidene bromide*, which are formed by substitution of two hydrogens of ethane with chlorine or bromine.

NOTE. — The addition of bromine to ethylene is illustrated by the experiment last performed, in which ethylene bromide is formed. To purify the product, put a little dilute caustic soda in the cylinder, and shake. Remove the upper layer of water, and repeat the washing with dilute caustic soda. Then wash with water two or three times, each time removing the water with the aid of the pipette described on p. 31. Finally, put the oil in a flask, add a few pieces of granulated calcium chloride, and allow to stand. Pour off into a dry distilling-bulb, and distil, noting the temperature.

A question which we may fairly ask concerning the structure of ethylene is this: Does it consist of two groups $CH_2$, or of a methyl group, $CH_3$, and CH? Is it to be represented by the formula $CH_2.CH_2$ or $CH_3.CH$? Perhaps the clearest answer to this question is found in the fact that the chloride formed by addition of chlorine to ethylene, and that formed by replacing the oxygen in aldehyde by chlorine, are not identical. All evidence is in favor of the view that aldehyde is correctly represented by the formula $CH_3.C^{O}_{H}$. Hence, as has been pointed out, the chloride obtained from it must be represented thus, $CH_3.CHCl_2$. Hence, further, it appears highly probable that the isomeric chloride obtained from ethylene must be represented thus, $CH_2Cl.CH_2Cl$. Now, as this substance is formed by direct addition of chlorine to ethylene, ethylene has the formula  $\begin{array}{c}CH_2\\ |\\ CH_2\end{array}$, and not  $\begin{array}{c}CH_3\\ |\\ CH\end{array}$.

As regards the relations between the two carbon atoms of ethylene we know nothing, save that it is probably different from that which exists between the carbon atoms of ethane. It is usually represented by the sign =; thus,  $\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}$. We must necessarily leave the question open as to the relation between the carbon atoms in ethylene. If the above sign is used, it should serve mainly as an indication of the kind of unsaturation met with in ethylene, the compound in whose formula it is written having the power to take up two atoms of bromine, a molecule of hydrobromic acid, etc.

The homologues of ethylene bear the same relation to it that the homologues of ethane bear to this hydrocarbon. Propylene is methyl-ethylene, $\begin{array}{c}CH.CH_3\\ |\\ CH_2\end{array}$, just as propane is methyl-ethane, $\begin{array}{c}CH_2.CH_3\\ |\\ CH_3\end{array}$. Butylene is dimethyl-ethylene, $\begin{array}{c}CH.CH_3\\ |\\ CH.CH_3\end{array}$, or $\begin{array}{c}C(CH_3)\\ |\\ CH_2\end{array}$, or ethyl-ethylene, $\begin{array}{c}CH.C_2H_5\\ |\\ CH_2\end{array}$. That is to say, in other words, in the hydrocarbons of the ethylene series the ethylene condition between carbon atoms occurs only once.

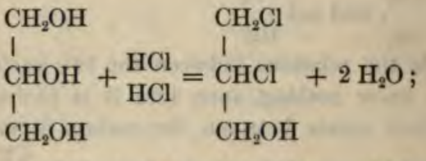
The higher members of the series need not be considered.

## ALCOHOLS, $C_nH_{2n}O$.

These alcohols bear to the ethylene hydrocarbons the same relation that the alcohols of the methyl alcohol series bear to the paraffins. Only one is well known. This is the second member corresponding to propylene.

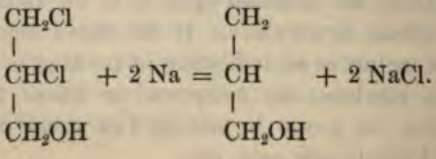
**Allyl alcohol, $C_3H_6O(= CH_2.CH.CH_2OH)$.**—This alcohol is formed in several ways from glycerin.

1. By introducing two chlorine atoms into glycerin in the place of two hydroxyls, thus getting dichlorhydrin, $C_3H_5Cl_2.OH$:



$$\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array} + \begin{array}{c}HCl\\ HCl\end{array} = \begin{array}{c}CH_2Cl\\ |\\ CHCl\\ |\\ CH_2OH\end{array} + 2\,H_2O;$$

and treating the dichlorhydrin with sodium, which extracts the chlorine:—



$$\begin{array}{c}CH_2Cl\\ |\\ CHCl\\ |\\ CH_2OH\end{array} + 2\,Na = \begin{array}{c}CH_2\\ |\\ CH\\ |\\ CH_2OH\end{array} + 2\,NaCl.$$

2. By treating glycerin with the iodide of phosphorus. This gives allyl iodide, $C_3H_5I$. By treating the iodide with silver hydroxide it is converted into the alcohol.

3. Most readily by treating glycerin with oxalic acid, as in the preparation of formic acid. The mixture is heated to 220° to 230°, when allyl alcohol passes over.

It is manufactured in this way on the large scale for the purpose of making artificial oil of mustard. The reactions involved are quite complicated.

Allyl alcohol is a liquid boiling between 99° and 100°. It has a penetrating odor.

Nascent hydrogen, from zinc and hydrochloric acid, converts it partially into propyl alcohol: —

$$C_3H_5.OH + H_2 = C_3H_7.OH.$$

The relation between allyl alcohol and propyl alcohol is the same as that between ethylene and ethane.

Allyl alcohol, like ethylene, unites directly with bromine, hydrobromic acid, etc., the products being substitution-products of propyl alcohol: —

$$C_3H_5.OH + HBr = \underset{\text{Monobrom-propyl alcohol.}}{C_3H_6Br.OH,}$$

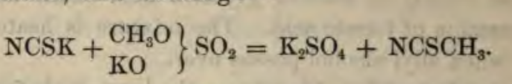
$$C_3H_5.OH + 2\,Br = \underset{\text{Dibrom-propyl alcohol.}}{C_3H_5Br_2.OH.}$$

**Allyl compounds.** — Among the derivatives of allyl alcohol which are of special interest is *allyl sulphide*, $(C_3H_5)_2S$, which is the chief constituent of the *oil of garlic*. It may be made artificially by treating allyl iodide with potassium sulphide: —

$$2\,C_3H_5I + K_2S = (C_3H_5)_2S + 2\,KI.$$

It is an oily liquid of a disagreeable odor.

**Allyl mustard oil, $SCN.C_3H_5$.** — Under the head of Sulpho-cyanates mention was made of a series of isomeric bodies called *isosulpho-cyanates* or *mustard oils*. The sulpho-cyanates of the alcohol radicals are made from potassium sulpho-cyanate. Thus, methyl sulpho-cyanate is made by mixing together potassium methyl-sulphate and potassium sulpho-cyanate, and distilling: —



$$NCSK + \left.\begin{matrix} CH_3O \\ KO \end{matrix}\right\} SO_2 = K_2SO_4 + NCSCH_3.$$

The mustard oils, on the other hand, are made by a complicated reaction from carbon bisulphide and substituted ammonias. The conduct of the sulpho-cyanates led us to the conclusion that they must be represented by the formula NC—SR, while that of the isosulpho-cyanates or mustard oils led to the formula SC—NR, as representing their structure. Allyl mustard oil is the chief representative of the class of bodies known as mustard oils. It occurs as a glucoside (see p. 178) in mustard seed. From the glucoside it is formed by fermentation. It is formed by treating allyl iodide with potassium sulpho-cyanate. We would naturally expect this reaction to yield allyl sulpho-cyanate, but the compound actually obtained does not conduct itself like the sulpho-cyanates.

Allyl mustard oil is a liquid, boiling at 150.7°, and having a penetrating odor.

With zinc and hydrochloric acid it is converted into allylamine, $NH_2.C_3H_5$, hydrogen sulphide and carbon dioxide. This reaction indicates that in allyl mustard oil the radical allyl is in combination with the nitrogen and not with the sulphur.

NOTE FOR STUDENT. — What change do the mustard oils in general undergo when treated with nascent hydrogen? What change do the sulpho-cyanates undergo under the same circumstances?

**Acroleïn, acrylic aldehyde, $C_3H_4O(=C_2H_3.COH)$.**—Acroleïn may be made by careful oxidation of allyl alcohol. It is formed by the dry distillation of glycerin which breaks up into water and acroleïn: —

$$C_3H_8O_3 = C_3H_4O + 2\,H_2O.$$

It is, hence, formed also by heating the ordinary fats, the peculiar penetrating odor noticed when fatty substances are heated to a sufficiently high temperature being due to the formation of acroleïn. It is prepared best by heating glycerin with acid potassium sulphate.

**Experiment 52.** In a test-tube mix anhydrous glycerin (1 part) and acid potassium sulphate (2 parts), and heat the mixture. Pass the vapors through a bent tube into water contained in another test-tube. Notice the odor. Try the effect on a dilute solution of nitrate of silver. What is the meaning of this reaction?

Acroleïn is a volatile liquid which boils at 52.4°. It has an extremely penetrating odor, and its vapor acts violently upon the eyes, causing the secretion of tears.

Acroleïn takes up oxygen from the air, and is converted into the corresponding acid, *acrylic acid*, $C_3H_4O_2$ (which see).

It takes up hydrogen, and is thus converted into allyl alcohol.

It takes up hydrochloric acid, and is converted into β-chlor-propionic aldehyde: —

$$C_2H_3.COH + HCl = \underset{\beta\text{-chlor-propionic aldehyde.}}{CH_2Cl.CH_2.COH}.$$

The first two reactions are characteristic of aldehydes in general; the last one is characteristic of unsaturated compounds belonging to the ethylene group. Acroleïn, like ordinary aldehyde, forms polymeric modifications, which can easily be reconverted into acroleïn.

It unites with ammonia forming acroleïn-ammonia, and with other substances in much the same way as ordinary aldehyde does.

## ACIDS, $C_nH_{2n-2}O_2$.

Running parallel to the ethylene series of hydrocarbons, and bearing the same relation to it that the fatty acid series bears to the paraffins, is a series of acids of which the first member is acrylic acid, $C_3H_4O_2$. Several members of the series are known. The principal members are named in the subjoined table: —

### ACRYLIC ACID SERIES.

ACIDS, $C_nH_{2n-2}O_2$.

| | | |
|---|---|---|
| Acrylic | acid | $C_3H_4O_2$. |
| Crotonic | " | $C_4H_6O_2$. |
| Angelic | " | $C_5H_8O_2$. |
| Hydrosorbic | " | $C_6H_{10}O_2$. |
| Teracrylic | " | $C_7H_{12}O_2$. |
| Cimic | " | $C_{15}H_{28}O_2$. |
| Hypogæic | " | $C_{16}H_{30}O_2$. |
| Oleïc | " | $C_{18}H_{34}O_2$. |
| Erucic | " | $C_{22}H_{42}O_2$. |

Of most of the higher members of the series several isomeric modifications are known. Only a few of these acids will be considered here.

**Acrylic acid, $C_3H_4O_2$($=CH_2.CH.CO_2H$).** — This acid has already been mentioned in connection with hydracrylic acid, which, when heated, breaks up into acrylic acid and water: —

$$\underset{\text{Hydracrylic acid.}}{CH_2.OH.CH_2.CO_2H} = \underset{\text{Acrylic acid.}}{CH_2.CH.CO_2H} + H_2O.$$

NOTE FOR STUDENT. — This reaction is analogous to that which takes place when ordinary alcohol is converted into ethylene. In what does the analogy consist? What acid is isomeric with hydracrylic acid? How does it conduct itself when heated? Compare the transformation of hydracrylic acid into acrylic acid with that of malic into maleïc and fumaric acids, and with that of citric into aconitic acid.

Acrylic acid may be made by careful oxidation of acroleïn *with silver* oxide. The relations between propylene, $C_3H_6$, allyl alcohol, $C_3H_5.OH$, acroleïn, $C_2H_3.COH$, and acrylic acid, $C_2H_3.CO_2H$, are the same as those between any hydrocarbon of the paraffin series, and the corresponding *primary* alcohol, aldehyde, and acid.

Acrylic acid may be made further by treating β-iodo-propionic acid with alcoholic potash: —

$$CH_2I.CH_2.CO_2H = CH_2.CH.CO_2H + HI.$$

NOTE FOR STUDENT. — Compare this reaction with that by which ethylene is made from ethyl bromide.

Acrylic acid is a liquid having a pungent odor. It boils at 140°, and solidifies at a low temperature.

Nascent hydrogen converts it into propionic acid. Hydriodic acid unites directly with it, forming β-iodo-propionic acid.

NOTE FOR STUDENT. — What are the analogous reactions with allyl alcohol and acroleïn?

Many derivatives of acrylic acid have been studied, but they need not be taken up here.

**Crotonic acid, $C_4H_6O_2$.** — Crotonic acid is made from allyl cyanide, the reactions involved being represented by the following equations: —

$$\underset{\text{Allyl iodide.}}{C_3H_5I} + KCN = \underset{\text{Allyl cyanide.}}{C_3H_5.CN} + KI;$$

$$C_3H_5.CN + 2\,H_2O = \underset{\text{Crotonic acid.}}{C_3H_5CO_2H} + NH_3.$$

It may be made also by distilling β-hydroxy-butyric acid, $CH_3.CH(OH).CH_2.CO_2H$, when a reaction takes place similar to that involved in the preparation of acrylic from hydracylic acid. Further, it may be made by treating α-brom-butyric acid with alcoholic potash.

**Oleïc acid, $C_{18}H_{34}O_2$.** — This acid was spoken of in connection with the fats, it being one of the three acids found most frequently in combination with glycerin. Oleïn, or glyceryl tri-oleate, is the liquid fat, and is the chief constituent of the fatty oils, such as olive oil, whale oil, etc. It is contained also in almost all ordinary fats. In the preparation of stearic acid for the manufacture of candles, the oleïn is pressed out of the fats. To prepare the acid, oleïn is saponified, and the soap then decomposed with hydrochloric acid.

NOTE FOR STUDENT. — Give the equations representing the reactions involved in passing from oleïn, or glyceryl tri-oleate, to oleïc acid.

Oleïc acid is a crystallized substance which melts at a low temperature (14°). It unites with bromine, forming bibromstearic acid. Hydriodic acid converts it into stearic acid: —

$$\underset{\text{Oleïc acid.}}{C_{18}H_{34}O_2} + H_2 = \underset{\text{Stearic acid.}}{C_{18}H_{36}O_2}.$$

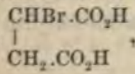
### POLYBASIC ACIDS OF THE ETHYLENE GROUP.

There are a few bibasic acids which bear to the ethylene hydrocarbons the same relations that the members of the oxalic acid series bear to the paraffins. They may be regarded as derived from the hydrocarbons by the introduction of two carboxyl groups.

**Acids, $C_2H_2(CO_2H)_2$.** — There are two acids of this formula, both of which have been mentioned. They are *fumaric* and *maleïc acids*, which are formed by the distillation of malic acid.

NOTE FOR STUDENT. — What is the reaction?

Fumaric acid may also be made by treating brom-succinic acid,

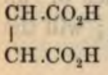


$$\begin{array}{l} CHBr.CO_2H \\ | \\ CH_2.CO_2H \end{array}$$

, with alcoholic potash.

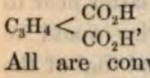
NOTE FOR STUDENT. — What is the reaction?

Both fumaric and maleïc acids are converted into succinic acid by nascent hydrogen, and into brom-succinic acid by hydrobromic acid. The character of the isomerism of these two acids is not understood. Their easy transformation into succinic acid and brom-succinic acid shows that the formula



$\begin{array}{l} CH.CO_2H \\ | \\ CH.CO_2H \end{array}$ applies to both of them.

**Acids, $C_5H_6O_4$.** — There are three acids of this formula, all of which are obtained, either directly or indirectly, from citric acid. They are known as *itaconic*, *citraconic*, and *mesaconic acids*. They bear the same relation to pyrotartaric acid,



$C_3H_4 < \begin{array}{l} CO_2H \\ CO_2H \end{array}$, that fumaric and maleïc acids bear to succinic acid. All are converted into pyrotartaric acid by treatment with nascent hydrogen.

**Aconitic acid, $[C_6H_6O_6 (= C_3H_3(CO_2H)_3)]$.** — Aconitic acid is the only tri-basic acid of this group that need be mentioned. As has been stated, it is formed when citric acid is heated to 175°. It is found in nature in aconite root, and in the sap of sugar-cane and of the beet.

Nascent hydrogen converts it into tri-carballylic acid, $C_3H_5(CO_2H)_3$.

## ACETYLENE AND ITS DERIVATIVES.

The principal reactions by means of which we are enabled to pass from a hydrocarbon of the paraffin series to the corresponding hydrocarbon of the ethylene series consist in introducing a halogen into the paraffin, and then treating the mono-halogen substitution-product with alcoholic potash: —

$$C_2H_5Br = C_2H_4 + HBr.$$

The effect of these two reactions is the abstraction of two hydrogen atoms from the paraffin. The following questions therefore suggest themselves: —

Suppose a bibrom substitution-product of a paraffin be heated with alcoholic potash; will the effect be that represented by the equation

$$C_2H_4Br_2 = C_2H_2 + 2\,HBr?$$

And, further, suppose a mono-substitution product of an ethylene hydrocarbon be treated with alcoholic potash; will the effect be that represented by the equation

$$C_2H_3Br = C_2H_2 + HBr?$$

If so, it is plain that we have it in our power to make a new series of hydrocarbons, the members of which shall bear to the ethylene hydrocarbons the same relation that the latter bear to the paraffins. The general formula of this series would be $C_nH_{2n-2}$, that of the ethylene series being $C_nH_{2n}$, and that of the paraffin series, $C_nH_{2n+2}$.

A few members of the hydrocarbon series, $C_nH_{2n-2}$, are known, though only one is well known, and only this one need be considered.

**Acetylene, $C_2H_2$.** — Acetylene is formed by direct combination of hydrogen and carbon when a current of hydrogen is passed between carbon poles, which are incandescent in consequence of the passage of an electric current; when alcohol, ether, and other organic substances are passed through a tube heated to redness; when coal gas and some other substances are burned in an insufficient supply of air; and when ethylene bromide is treated with alcoholic potash: —

$$C_2H_4Br_2 = C_2H_2 + 2\,HBr.$$

It may be prepared most conveniently by the incomplete combustion of coal gas.

**Experiment 53.** — Light a Bunsen burner at the base, and turn it down so that the flame is small. The condition is the same as that observed when a burner "strikes back." The odor noticed, which is familiar to every one who has worked in a chemical laboratory, is that of acetylene, which is mixed with the products given off from the burner. To collect the gas, arrange an apparatus as shown in Fig. 13. Place the glass funnel over the burner, from which acetylene is given off. In *B* put a strong solution of ammoniacal cuprous chloride prepared as follows: Make a saturated solution of 1 part common salt and 2½ parts crystallized copper sulphate. Saturate with sulphur dioxide. Filter, and wash with acetic acid. Dissolve the white cuprous chloride in ammonia.

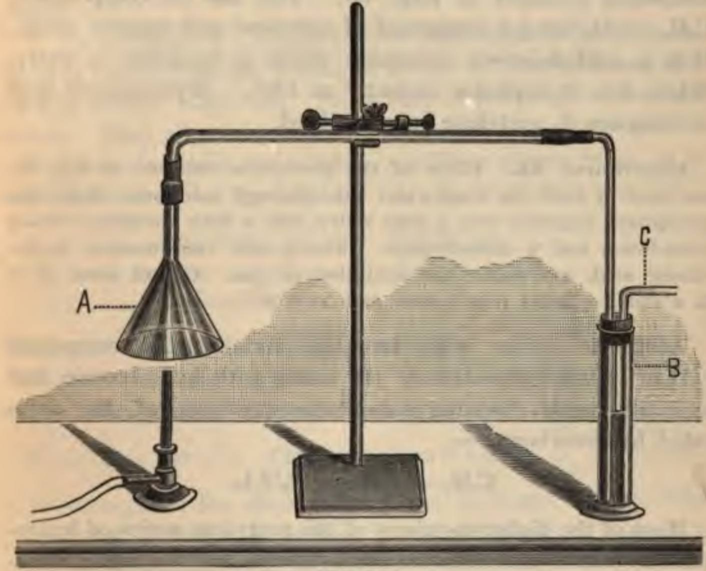


Fig. 13.

Connect the apparatus at *C* with some kind of aspirator (suction-pump, a gasometer filled with water, etc.), and draw the gases slowly through the solution. The acetylene will be absorbed by the copper solution, and a precipitate formed (see Exp. 54).

Acetylene is a gas of an unpleasant odor. It burns with a luminous, sooty flame.

When heated to a sufficiently high temperature, it is converted into the polymeric substances, benzene, $C_6H_6$, and styrene, $C_8H_8$. It unites with hydrogen to form ethylene and ethane. It unites with nitrogen, under the influence of the sparks from an induction coil, forming hydrocyanic acid: —

$$C_2H_2 + 2\,N = 2\,HCN.$$

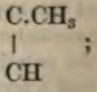
Acetylene forms some curious compounds with metals and metallic oxides. Among them may be mentioned the copper compound obtained in Exp. 53. This has the composition, $C_2H_2 . Cu_2O$, being a compound of acetylene and cuprous oxide. It is a reddish-brown substance which is insoluble in water. When dry, it explodes violently at 120°. Hydrochloric acid decomposes it, acetylene being evolved.

**Experiment 54.** Filter off the precipitate obtained in Exp. 53, and wash it until the wash-water runs through colorless. Bring the precipitate, together with a little water, into a flask furnished with a funnel-tube and a delivery-tube. Slowly add concentrated hydrochloric acid, and notice the evolution of gas. Collect some of it in a small cylinder over water, and burn it.

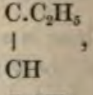
Acetylene unites with bromine, forming the compound $C_2H_2Br_4$, tetra-brom-ethane. It unites with hydrobromic and hydriodic acids, forming substitution-products of the saturated hydrocarbons: —

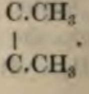
$$C_2H_2 + 2\,HI = C_2H_4I_2.$$

Most of the higher members of the acetylene series of hydrocarbons bear to acetylene the same relation that the higher members of the ethylene series bear to ethylene. The first one is

*Allylene* or *methyl-acetylene* . . . .

$$\begin{array}{l} C.CH_3 \\ \mid \\ CH \end{array} ;$$

the second is

*Ethyl-acetylene* . . . . . . . . . .

$$\begin{array}{l} C.C_2H_5 \\ \mid \\ CH \end{array} ,$$

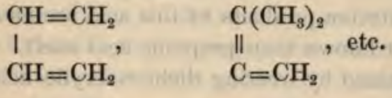
or *Dimethyl-acetylene* . . . . . . . .

$$\begin{array}{l} C.CH_3 \\ \mid \\ C.CH_3 \end{array} .$$

It should be noticed in this connection that there is a hydrocarbon of the formula $C_4H_6$, which, strictly speaking, is not a homologue of acetylene, though it is very closely allied to dimethyl-acetylene. It has the formula $\begin{array}{l} CH=CH_2 \\ | \\ CH=CH_2 \end{array}$.

The homologues of acetylene may be divided into two classes: —

1. Those which are obtained from acetylene by the replacement of one or both the hydrogen atoms by saturated radicals, such as methyl, ethyl, etc. These may be called the *true homologues*. They all retain the condition peculiar to acetylene.

2. Those in which the ethylene condition occurs twice, as in the hydrocarbons of the formulas



$$\begin{array}{l} CH=CH_2 \\ | \\ CH=CH_2 \end{array}, \qquad \begin{array}{l} C(CH_3)_2 \\ \| \\ C=CH_2 \end{array}, \text{ etc.}$$

These may be called *diethylene derivatives*.

We know nothing regarding the relation between the carbon atoms in acetylene. It is commonly represented by three lines ($\equiv$), or three dots ($\vdots$). Thus, acetylene is written $\begin{array}{c} CH \\ ||| \\ CH \end{array}$ or $CH \vdots CH$. Like the sign for the ethylene condition, it should not be interpreted too literally. It is best to regard it as the sign of a condition best illustrated in acetylene, and which may therefore be called the *acetylene condition*. *We recognize this condition in a compound by the power of the compound to take up four atoms of a halogen, or two molecules of hydrobromic acid and similar acids;* though, as we have seen, these reactions are not distinctive for the acetylene condition, for the reason that the diethylene compounds have the same power.

**Propargyl alcohol,** $C_3H_4O$. — This alcohol is mentioned merely as an example of alcohols which are derived from the acetylene hydrocarbons. It is the hydroxyl derivative of allylene, or methyl-acetylene. It is made by treating brom-allyl alcohol, $C_3H_4Br.OH$, with alcoholic potash:—

$$C_2H_4Br.OH = C_3H_2.OH + HBr.$$

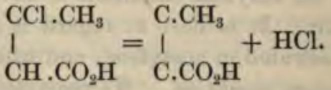
### ACIDS, $C_nH_{2n-4}O_2$.

These acids are the carboxyl derivatives of the acetylene hydrocarbons, and hence differ from the members of the acrylic acid series by two atoms of hydrogen each, and from the members of the fatty acid series by four atoms of hydrogen each.

**Propiolic acid,** $C_3H_2O_2\left(=\begin{array}{l}CH\\ \vert\\ C.CO_2H\end{array}\right)$.—The bromine and chlorine substitution-products of this acid are more easily made and are better known than propiolic acid itself. Chlor-propiolic acid is obtained by treating dichlor-acrylic acid with baryta water:—

$$C_2HCl_2.CO_2H = C_2Cl.CO_2H + HCl.$$

**Tetrolic acid,** $C_4H_4O_2\left(=\begin{array}{l}C.CH_3\\ \vert\\ C.CO_2H\end{array}\right)$, is obtained by treating $\beta$-chlor-crotonic acid with caustic potash:—



$$\begin{array}{l}CCl.CH_3\\ \vert\\ CH.CO_2H\end{array} = \begin{array}{l}C.CH_3\\ \vert\\ C.CO_2H\end{array} + HCl.$$

**Sorbic acid,** $C_6H_8O_2(= C_5H_7.CO_2H)$.—This acid occurs in the unripe berries of the mountain ash. It takes up hydrogen and yields *hydrosorbic acid*, a member of the acrylic acid series (see table, p. 218). It also takes up bromine, the final product of the action being an acid of the formula $C_5H_7Br_4.CO_2H$. With hydrobromic acid it forms dibrom-caproic acid:—

$$C_5H_7.CO_2H + 2\,HBr = \underset{\text{Dibrom-caproic acid.}}{C_5H_9Br_2.CO_2H}.$$

**Leinoleïc acid, $C_{16}H_{28}O_2(=C_{15}H_{27}.CO_2H)$.**—This acid occurs in the form of an ethereal salt of glycerin in *linseed oil*. It may be obtained from linseed oil by saponification. It is an oily liquid, one of the most marked properties of which is its power to take up oxygen from the air, being thus transformed into a solid substance. Linseed oil itself has this property of hardening or drying. It is the principal substance belonging to the class of *drying oils*. The oil is used extensively as a constituent of varnishes and of oil paints.

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**Valylene, $C_5H_6$.** — We have thus far had to deal with three series of hydrocarbons of the general formulas $C_nH_{2n+2}$, $C_nH_{2n}$, and $C_nH_{2n-2}$. We naturally inquire whether there is a series of the general formula $C_nH_{2n-4}$. A few members of the series have been prepared by abstracting hydrogen from certain of the acetylene hydrocarbons by the action of alcoholic potash on the bromine derivatives. Thus, *valylene*, $C_5H_6$, has been made by treating valerylene bromide, $C_5H_8Br_2$, with alcoholic potash: —

$$C_5H_8Br_2 = C_5H_6 + 2\,HBr.$$

It is a liquid. Its most characteristic property is its power to unite with bromine to form the saturated compound $C_5H_6Br_6$.

**Dipropargyl, $C_6H_6$.** — Dipropargyl is obtained from the compound dibrom-diallyl, $C_6H_8Br_2$, by boiling with alcoholic caustic potash: —

$$C_6H_8Br_2 = C_6H_6 + 2\,HBr.$$

It unites very readily with bromine, forming, as the final product of the action, the compound $C_6H_6Br_8$, which is an octo-bromine substitution-product of hexane, $C_6H_{14}$.

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The unsaturated hydrocarbons and their derivatives thus far considered are obtained by simple reactions from the saturated compounds, and they all have the power to take up readily bromine, hydrobromic acid, etc., and thus to pass back to the saturated condition. Whatever the real nature of the relation between the carbon atoms in all these unsaturated hydrocarbons may be, it certainly is easily changed to the condition which exists in the saturated compounds. There are several hydrocarbons, however, which are unsaturated but which are not easily converted into derivatives of the saturated hydrocarbons. Although under some circumstances they with difficulty unite directly with the halogens, they do not take up enough to convert them into derivatives of the paraffins; and the products which are formed are unstable, easily giving up the halogen atoms with which they united. The simplest hydrocarbon of this new kind is the well-known benzene, which is isomeric with dipropargyl. Before proceeding to the consideration of benzene and its derivatives, it will be well to inquire whether the abstraction of hydrogen by the reaction chiefly used can be pushed further than it has thus far been pushed. Can we, in other words, by means of this reaction get hydrocarbons of the formula $C_nH_{2n-8}$ which have the power to unite directly with ten atoms of bromine? Such hydrocarbons have not been prepared. Hydrocarbons of the formula $C_nH_{2n-8}$ are known; but they are not made from the paraffins by abstracting hydrogen, and they are not converted into substitution-products of the paraffins by the addition of halogens and halogen acids. The compounds which have been considered fall under five general heads, according to the formulas of the hydrocarbons. These heads are, —

1. *Hydrocarbons*, $C_nH_{2n+2}$, *the paraffins and their derivatives.*
2. *Hydrocarbons*, $C_nH_{2n}$, *or olefins and their derivatives.*
3. *Hydrocarbons*, $C_nH_{2n-2}$, *or the acetylene hydrocarbons and their derivatives.*
4. *Hydrocarbons*, $C_nH_{2n-4}$, *and their derivatives.*
5. *Hydrocarbons*, $C_nH_{2n-6}$, *and their derivatives.*

This classification, while strictly correct, is misleading, inasmuch as it conveys no idea in regard to the relative importance of the compounds of the different classes. As we have seen, the only compounds whose treatment required much time are those of the first class. These compounds stand out prominently, and are distinguished by the frequency of their occurrence and their great number. The compounds of the second class are much less numerously represented, and but a small number of them are familiar substances. While a few substances belonging to the third class are known, our knowledge in regard to the class is much more limited than even that of the second class. Finally, as regards the fourth and fifth classes, the few representatives of them that are known are at present scientific curiosities. Thus, after we leave the paraffin derivatives, our knowledge dwindles away very rapidly when we pass to the following classes, until it ends with a single compound in the fifth class.

We pass now to the consideration of a new group, the importance and number of whose members entitle it to be placed side by side with the group of paraffin derivatives.

# CHAPTER XIV.

## THE BENZENE SERIES OF HYDROCARBONS.—AROMATIC COMPOUNDS.

THE fundamental substance of this group is benzene, $C_6H_6$, which bears to the group the same relation that marsh gas bears to the group of paraffin derivatives. Benzene, together with some of its homologues, is a product of the distillation of bituminous coal, and is, therefore, contained in *coal tar*. As coal tar is the raw material from which all benzene derivatives are obtained, it will be well briefly to consider the conditions of its formation and the method of obtaining pure hydrocarbons from it.

**Coal tar** is a thick, black, tarry liquid, which is obtained in the manufacture of illuminating gas from bituminous coal. The coal is heated in retorts, and all the products passed through a series of tubes called *condensers*. These are kept cool, and in them the liquid and volatile solid products are condensed, forming together the coal tar. It is an extremely complex mixture, from which a great many substances have been obtained. Among those most readily obtained from it are the hydrocarbons of the benzene series, as well as the hydrocarbons naphthalene and anthracene, both of which are important substances.

When the tar is heated, of course the most volatile liquids pass over first. These are collected in vessels containing water. The first portions of the distillate float on water, and constitute what is called the *light oil*. After a time hydrocarbons and other substances of greater specific gravity than the light oil pass over. These portions sink under water, and constitute the *heavy oil.*

The light oil is treated with caustic soda, which removes phenol (carbolic acid) and similar substances, and with sulphuric acid, which removes certain basic compounds. The residue is then subjected to fractional distillation, by which means the first two members of the series can be obtained in very nearly pure condition. As these hydrocarbons form the basis of a number of important industries, they are separated from coal tar on the large scale.

The principal members of the series are named in the table below.

### HYDROCARBONS, $C_nH_{2n-6}$.

### BENZENE SERIES.

| | |
|---|---|
| Benzene | $C_6H_6$. |
| Toluene | $C_7H_8$. |
| Xylene | $C_8H_{10}$. |
| Mesitylene<br>Pseudocumene | $C_9H_{12}$. |
| Durene<br>Cymene | $C_{10}H_{14}$. |
| Hexa-methyl benzene | $C_{12}H_{18}$. |

**Benzene, $C_6H_6$.** — Benzene is prepared, as above described, from the light oil obtained from coal tar. It is also prepared by treating benzoic acid with lime, when the acid breaks up into carbon dioxide and benzene: —

$$C_7H_6O_2 = C_6H_6 + CO_2.$$

NOTE FOR STUDENT. — What is the analogous method for the preparation of marsh gas?

Benzene has been made further by simply heating acetylene:

$$3\ C_2H_2 = C_6H_6.$$

To purify the hydrocarbon obtained by fractional distillation from light oil, it is cooled down to a low temperature, and that which does not solidify is poured off. The crystals are pressed in the cold between layers of bibulous paper, and are then very nearly pure benzene. This may be further purified by treatment with sulphuric acid, which removes a small quantity of a substance containing sulphur, and known as *thiophene*. Perfectly pure benzene is obtained by distilling pure benzoic acid with lime.

**Experiment 55.** Mix intimately $50^g$ benzoic acid and $100^g$ quicklime, and distil from a flask connected with a condenser. See that the materials and apparatus are dry. Add a little calcium chloride to the distillate; and, after it has stood for an hour or two, redistil it from an appropriate sized distilling-bulb, noting the temperature at which it boils. Put the redistilled hydrocarbon in a test-tube, and surround it with a freezing mixture.

**Experiment 56.**—In most places where there are gas-works it will not be difficult to get a quantity of light oil. The separation of some of this into benzene and toluene, and the purification of the two hydrocarbons, is the best possible introduction to a study of the aromatic compounds. The benzene and toluene thus obtained may be used in the preparation of a number of typical derivatives according to methods which will be described. In fractioning the light oil, it will be observed that there is a tendency to an accumulation of the distillates in the parts boiling near 80° (the boiling-point of benzene) and 110° (the boiling-point of toluene). The final purification of the benzene should be effected by freezing and pressing, as described above. The toluene should be distilled until by redistillation its boiling-point is not changed.

Benzene is a colorless liquid which boils at 80.5°. It has a peculiar, pleasant odor. Several of the homologues of benzene have a similar odor. Hence the name *aromatic compounds* was given to them originally, and it is still in general use. Benzene is lighter than water, its specific gravity being 0.899 at 0°. It burns with a bright, luminous flame:

**Experiment 57.**—Pour a layer of benzene on water in a small evaporating-dish. Set fire to it.

At 0° benzene solidifies, forming rhombic prisms. It is an excellent solvent for oily and resinous substances.[1]

*Chemical conduct of benzene, and hypothesis regarding its structure.* In the light of the knowledge we have already gained in studying hydrocarbons which contain a smaller proportion of hydrogen than the paraffins do, we would naturally expect to find that benzene can easily be converted into a derivative of hexane. We would naturally expect to find that it unites with bromine, just as dipropargyl does, to form an octo-brom-hexane thus, —

$$C_6H_6 + Br_8 = C_6H_6Br_8;$$

with hydrobromic acid to form tetra-brom-hexane thus, —

$$C_6H_6 + 4\,HBr = C_6H_{10}Br_4;$$

and probably with hydrogen to form hexane, —

$$C_6H_6 + 8\,H = C_6H_{14}.$$

But none of these reactions takes place. Hydrobromic acid, which acts so readily on all the unsaturated compounds hitherto considered, does not act at all upon benzene. Bromine acts readily enough, but the action which usually takes place is like that which takes place with the saturated paraffins. It is *substitution, and not addition.* Thus, bromine forms mono-brom-benzene, $C_6H_5Br$, under ordinary circumstances. If, however, the action takes place in the direct sunlight, a product is formed which has the formula $C_6H_6Br_6$, known as *benzene hexabromide*, and to this no more bromine can be added. Further, benzene hexabromide is an unstable compound, — much less stable than benzene. When heated, it breaks up, partly according to the equation

$$C_6H_6Br_6 = C_6H_3Br_3 + 3\,HBr,$$

---

[1] Benzene, the chemical individual of the definite formula $C_6H_6$, must not be confounded with "benzine," the commercial substance obtained in the refining of petroleum (see p. 110).

the chief product being a substitution-product of benzene,—tri-brom-benzene, $C_6H_3Br_3$.

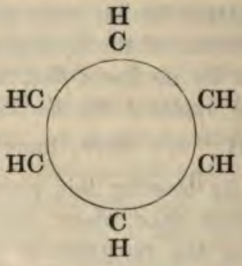
Treated with hydriodic acid, benzene takes up six atoms of hydrogen, and yields a hydrocarbon, $C_6H_{12}$, which, however, does not act like a member of the ethylene series, as it appears to have no power to take up bromine, etc., and shows a marked tendency to pass back into benzene, particularly under the influence of oxidizing agents.

The facts mentioned show clearly that benzene differs in some way fundamentally from all the hydrocarbons which have been considered. But these facts are not sufficient to enable us to form a hypothesis in regard to its structure. On studying the many substitution-products of benzene, however, we soon become acquainted with facts of a different order and of the highest importance.

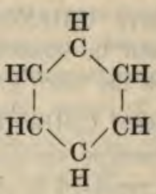
It will be remembered that our theory in regard to the relations of the paraffins to each other is based upon the fact, that only one mono-substitution product of marsh gas can be obtained with any given substituting agent. There is but one chlor-methane, but one brom-methane, etc. This fact leads us to believe that each hydrogen atom of marsh gas bears the same relation to the carbon atom, or that marsh gas is a symmetrical compound. A similar conclusion has been reached in regard to benzene; and it is based upon a most exhaustive study of the substitution-products. Notwithstanding almost innumerable efforts to prepare isomeric mono-substitution products of benzene, no such isomeric substances have been prepared. There is but one mono-brom-benzene, but one mono-chlor-benzene, etc., etc. Further, mono-brom-benzene has been prepared by replacing the six hydrogen atoms of benzene successively by bromine; and the product has been found to be the same, no matter which hydrogen is replaced. As this fact is of fundamental importance, it will be well to consider how it is possible to replace the six hydrogens successively, and to know that in *each* case a different hydrogen atom is replaced. While it would lead us too far to consider this subject in detail, the principle made use of can be made clear in a few words: —

We have a compound, the formula of which is $C_6H_6$. Write it thus, $C_6\overset{1}{H}\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, numbering the hydrogen symbols to facilitate reference to them. The problem is to replace, say $\overset{1}{H}$, by bromine; in a second case, to replace $\overset{2}{H}$ by bromine; in a third, $\overset{3}{H}$, etc; and to compare the six mono-brom-benzenes thus obtained. Suppose we treat benzene with bromine. We get a mono-brom-benzene, and we know that one of the hydrogen atoms is replaced by bromine, but of course we cannot tell which one. We may assume that it is any one of the six represented in the above formula. For the sake of the argument, call it $\overset{1}{H}$. Our compound is therefore $C_6Br\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. Now treat this compound with something else which has the power to replace the hydrogen, say nitric acid. A second hydrogen atom is replaced by the nitro group $NO_2$. Again, we do not know which one of the hydrogen atoms is replaced in this operation, *but we do know that it is a different one from that which was replaced by the bromine in the first operation.* Call it $\overset{2}{H}$. We have, therefore, the compound $C_6Br(NO_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. By treating this compound with nascent hydrogen, two reactions take place, the chief one for our present purpose being the replacement of the bromine by hydrogen. In other words, $\overset{1}{H}$ is put back into the compound again, and we have $C_6\overset{1}{H}(NO_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. By means of two reactions which will be considered a little later it is a simple matter to replace the nitro group by bromine. This done, we have the compound $C_6\overset{1}{H}Br\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, or a mono-brom-benzene, in which the bromine certainly replaces a different hydrogen atom from that replaced by direct substitution. The two products are, however, identical. The above explanation will serve to make the principle clear which is involved in the study of the relations which the hydrogen atoms contained in benzene bear to the molecule. The principle has been applied successfully to all the hydrogen atoms, and, as already stated, the result is the proof that all these hydrogen atoms bear the same relation to the molecule.

Thus far we have formed no conception in regard to the relations existing between the constituents of benzene. Can we, on the basis of the facts above stated, form any satisfactory conception in regard to these relations? How can we imagine six carbon atoms and six hydrogen atoms arranged so that all the latter shall bear the same relation to the molecule? The simplest conception is that each carbon is in combination with one hydrogen, and that the six carbon atoms are arranged in the form of a ring, and not, as in the paraffins, in the form of an open chain, or a chain with branches. Using our ordinary method of representation, this conception is symbolized in the formula



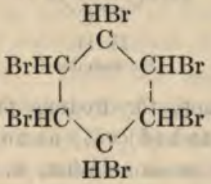
or, as the curved lines have no special significance, the expression becomes



This symbol, then, is the expression of a thought which is suggested by a study of the chemical conduct of benzene.

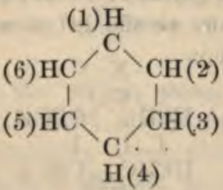
Before we can accept it as probable, it must first be tested by all the facts known to us. If it is not in accordance with all of them, if it suggests possibilities which are not realized, then it must be discarded, and we must form some other conception in regard to the structure of benzene.

In the first place, then, does it account for the addition products, benzene hexabromide, hexa-hydro-benzene, etc.? The formula represents each carbon atom as trivalent, and we would expect, therefore, that each one could take up an additional univalent atom, forming, in the case of bromine, a compound of the formula



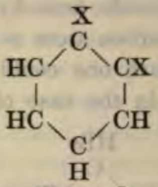
in which each carbon atom is acting as a quadrivalent atom. Unless the ring form of combination between the carbon atoms is broken up, it is impossible for the compound to take up more bromine. Hence, the last product of the addition of bromine to benzene should be benzene hexabromide; and, in the same way, the last product of the addition of hydrogen should be hexa-hydro-benzene, as it is. The facts and the hypothesis are in harmony.

Again, we may inquire: Of how many isomeric bi-substitution products of benzene does the hypothesis suggest the existence? Numbering the hydrogens in the formula, we have: —



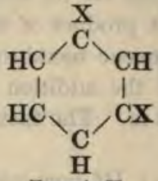
The hydrogens (1) and (2), (2) and (3), (3) and (4), (4) and

(5), (5) and (6), and (6) and (1), bear the same relations to each other; and, according to the formula, whether we replace (1) and (2), or (2) and (3), or (3) and (4), or any other of the above-named pairs, the product ought to be the same. We would get a compound of which the following is the general expression, in which X represents any substituting atom or group: —



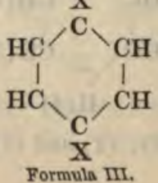
Formula I.

In the second place, the hydrogens (1) and (3), (2) and (4), (3) and (5), (4) and (6), (5) and (1), and (6) and (2) bear to each other the same relation, but a different relation from that which the above pairs do. Replacing any such pair, we would have a second compound, which is represented by the general formula



Formula II.

Finally, there is a third kind of relation, which is that between hydrogens (1) and (4), (2) and (5), and (3) and (6); and, by replacing such a pair, we should get a compound represented by the general formula

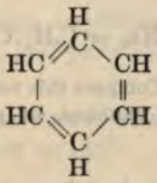


Formula III.

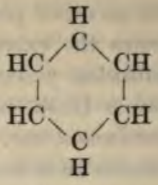
The hypothesis suggests no other possibilities. We see thus that the hypothesis indicates the existence of three, and only three, classes of bi-substitution products of benzene. There ought to be three, and only three, bi-chlor-benzenes; three, and only three, bi-brom-benzenes, etc.

The bi-substitution products have been studied very exhaustively for the purpose of determining definitely whether the conclusion above reached is in accordance with the facts; and it may be said at once, that every fact thus far discovered is in harmony with the hypothesis. Three well-marked classes of isomeric bi-substitution products of benzene are known, and only three; and many representatives of the three classes have been studied carefully. There are many other facts of less importance known which furnish arguments in favor of the benzene hypothesis expressed in the formula above discussed, but this is not the place to consider them. Let it suffice, for the present, to recognize that the hypothesis is in accordance with the most important facts known to us.

There is one point which has not been touched upon, and that is the relation of the carbon atoms to each other. In regard to this, as well as to the relation between the carbon atoms in ethylene and acetylene, we know nothing. The formula is commonly written thus: —



which indicates that the carbon atoms are joined together alternately by simple and by double bonds. This formula, however, expresses something about which we know nothing, and concerning which it is difficult, at present, to form any conception. The simple formula



leaves the question as to the relation between the carbon atoms entirely open, as it is in fact.

The benzene hypothesis has thus been considered pretty fully for the reasons, that it has played an extremely important part in the study of the benzene derivatives, that its use serves greatly to simplify the study of these derivatives, and that in most text-books, whether elementary or advanced, the hypothesis is merely stated, while the student is left to find out for himself its meaning, and this he generally fails to do. We may now return to a study of the facts upon which the hypothesis is founded, and of which the formula is the symbolic expression.

**Toluene, $C_7H_8(=C_6H_5.CH_3)$.** — Toluene was known before it was obtained from coal tar, as it is formed by the dry distillation of Tolu balsam, whence its name. Its relation to benzene is shown by its synthesis from brom-benzene and methyl iodide: —

$$C_6H_5Br + CH_3I + Na_2 = C_6H_5.CH_3 + NaBr + NaI.$$

NOTE FOR STUDENT. — Compare this reaction with that used in the synthesis of ethane from methane, of propane from ethane and methane, etc.

According to this synthesis, toluene appears as *methyl-benzene*, or benzene in which one hydrogen is replaced by methyl; or as *phenyl-methane*, or methane in which one hydrogen atom is replaced by the radical phenyl, $C_6H_5$, which bears the same relation to benzene that methyl bears to marsh gas.

Toluene is a colorless liquid which boils at 110°; has the specific gravity 0.8824 at 0°; and has a pleasant aromatic odor.

It is very susceptible to the action of reagents yielding a large number of substitution-products, some of the most important of which will be considered farther on.

But one toluene or methyl-benzene has ever been discovered.

Towards oxidizing agents its conduct is peculiar and interesting. The methyl is oxidized, while the phenyl remains intact. The product is a well-known acid, benzoic acid, which, as we have seen, breaks up readily into carbon dioxide and benzene. It has the composition $C_7H_6O_2$, and is the carboxyl derivative of benzene, $C_6H_5.CO_2H$. The oxidation of toluene is represented by the equation

$$C_6H_5.CH_3 + 3\,O = C_6H_5.CO_2H + H_2O.$$

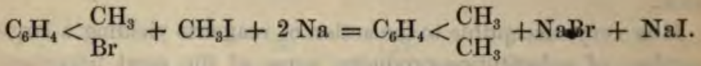
**Xylenes,** $C_8H_{10}[= C_6H_4(CH_3)_2]$. — That portion of light oil which boils at about 140° was originally called *xylene*. It was afterwards found that this coal-tar xylene consists of three isomeric hydrocarbons. As the boiling-points of these three substances lie quite near together, it is impossible to separate them by means of fractional distillation. By treatment with sulphuric acid, however, they may be separated, and thus obtained in pure condition. They are known as *ortho-xylene*, *meta-xylene*, and *para-xylene*.

**Ortho-xylene** resembles benzene and toluene in its general properties, but boils at 142° to 143°.

**Meta-xylene** boils at 139.8°.

**Para-xylene** boils at 136° to 137°.

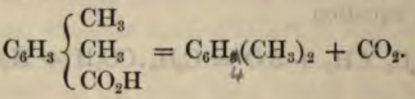
These hydrocarbons have also been obtained from toluene by means of the reaction made use of for the purpose of converting benzene into toluene:—



$$C_6H_4<{}^{CH_3}_{Br} + CH_3I + 2\,Na = C_6H_4<{}^{CH_3}_{CH_3} + NaBr + NaI.$$

This shows that they are all *methyl-toluenes.* There are three mono-brom-toluenes, known as ortho-, meta-, and para-brom-toluene. For the preparation of ortho-xylene, ortho-brom-toluene is used; meta-brom-toluene yields meta-xylene, and para-brom-toluene yields para-xylene.

Ortho- and meta-xylene have also been obtained from certain acids, which bear to them the same relation that benzoic acid bears to benzene:—



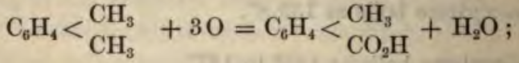
$$C_6H_3\begin{cases} CH_3 \\ CH_3 \\ CO_2H \end{cases} = C_6H_4(CH_3)_2 + CO_2.$$

The reaction by which *meta-xylene* is formed from *mesitylenic acid* is of special importance, as will be pointed out.

By oxidation, the xylenes undergo changes like that which is illustrated in the formation of benzoic acid from toluene, and which consists in the transformation of methyl into carboxyl. The first change gives acids of the formula $C_6H_4<{}^{CH_3}_{CO_2H}$, one corresponding to each xylene. By further oxidation, these three monobasic acids are converted into bibasic acids of the formula $C_6H_4<{}^{CO_2H}_{CO_2H}$. Thus, we have the three reactions, all of the same kind:—

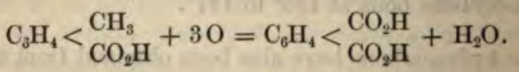
(1) $C_6H_5.CH_3 + 3\,O = C_6H_5.CO_2H + H_2O;$

(2)

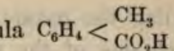


$$C_6H_4<{}^{CH_3}_{CH_3} + 3\,O = C_6H_4<{}^{CH_3}_{CO_2H} + H_2O;$$

and (3)

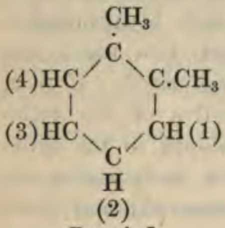


$$C_3H_4<{}^{CH_3}_{CO_2H} + 3\,O = C_6H_4<{}^{CO_2H}_{CO_2H} + H_2O.$$

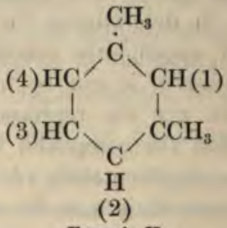
The three monobasic acids of the formula  $C_6H_4<\begin{matrix}CH_3\\CO_2H\end{matrix}$ are known as *ortho-toluic*, *meta-toluic*, and *para-toluic* acids respectively; and the three bibasic acids obtained from them are known as *ortho-phthalic*, *meta-phthalic*, and *para-phthalic* acids. Starting thus from the three brom-toluenes, we get, first, three xylenes, then three toluic acids, and finally three phthalic acids. In each case, we distinguish between the three isomeric compounds by the prefixes *ortho*, *meta*, and *para*. In a similar way, all bi-substitution products of benzene are designated. We therefore have three series into which all bi-substitution products of benzene can be arranged; and these are known as the *Ortho-series*, the *Meta-series*, and the *Para-series*. In arranging them in this way, we may select any prominent bi-substitution product, and call it an *ortho compound;* and then call one of its isomerides a *meta compound*, and the other a *para compound*. Having thus a representative of each of the three classes, the remainder of the problem consists in determining for each bi-substitution product, by means of appropriate reactions, into which one of the three representatives it can be transformed. If from a given compound we get the representative of the ortho series, we conclude that the compound belongs to the ortho series; if we get the representative of the meta series, we conclude that the compound is a meta compound; and if we get the representative of the para series, we conclude that the compound is a para compound. As representatives, we may select either the three xylenes or the three phthalic acids. Now, to repeat, any bi-substitution product of benzene which can be converted into ortho-xylene or into ortho-phthalic acid is regarded as an ortho compound, etc.

This classification of the bi-substitution products of benzene into the ortho, meta, and para series, by means of chemical transformations, is entirely independent of any hypothesis regarding the nature of benzene. We may now ask, however, which one of the three general expressions given above (see formulas I., II., and III., p. 238) represents the relation of the groups in the ortho compounds, which one the relation in the meta compounds, and which one the relation in the para compounds. If we can answer these questions for any three isomeric bi-substitution products, the answer for the rest will follow. To reduce the problem to simple terms, therefore, let us take the three xylenes. We have three xylenes and three formulas: how can we determine which particular formula to assign to each xylene?

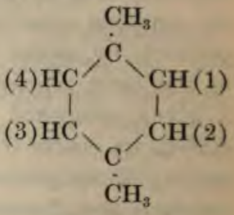
As may be imagined, this determination is by no means a simple matter; and it has been the occasion of a great many investigations. Theoretically, the simplest method available consists in carefully studying the substitution-products of each xylene, to discover how many varieties of mono-substitution products can be obtained from each. The formulas are:—



Formula I.



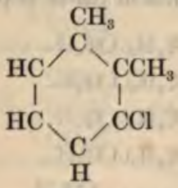
Formula II.



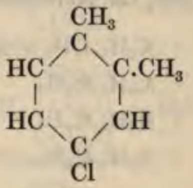
Formula III.

Each of the four unreplaced benzene hydrogens of the xylene of formula III. bears the same relation to the molecule. It therefore should make no difference which one is replaced, the product ought to be the same. This should not be true of the xylenes represented by formulas I. and II. That xylene, whose structure is represented by formula III., ought therefore to yield but one kind of mono-substitution product. On studying the xylenes, we find the one which boils at 136° to 137°, called para-xylene, yields but one kind of mono-substitution products; that is, we can get from it only one mono-brom-xylene; only one mono-nitro-xylene, etc. We therefore conclude that para-xylene is represented by formula III. above; and, further, that formula III., on p. 238, is the general expression for all para compounds.

Examining formula I., on the preceding page, in the same way, we see that H(1) and H(4) bear the same relation to the molecule; and that H(3) and H(2) also bear the same relation to the molecule, though different from that of H(1) and H(4). Two chlor-xylenes of the formulas



and



ought to be obtainable from the xylene of formula I.

In the same way three mono-substitution products might be obtainable from the xylene of formula II. The method, the principle of which is thus indicated briefly, while theoretically simple enough, is very difficult in its application, except in the case of the para compounds. Other methods have therefore been used, and these will be considered under mesitylene and naphthalene. It may be said, in anticipation, that the result of all observations point to formula I. for ortho-xylene; to formula II. for meta-xylene, and to formula III. for para-xylene.

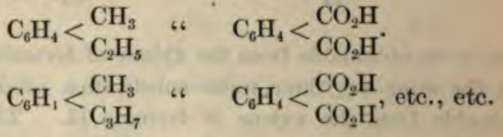
**Ethyl-benzene,** $C_8H_{10}(=C_6H_5.C_2H_5)$. — This hydrocarbon is isomeric with the xylenes, but differs from them in that it contains an ethyl group in the place of one hydrogen of benzene, instead of two methyl groups in the place of two hydrogens of benzene.

It is made by treating a mixture of brom-benzene and ethyl bromide with sodium: —

$$C_6H_5Br + C_2H_5Br + 2\,Na = C_6H_5.C_2H_5 + 2\,NaBr.$$

Its conduct towards oxidizing agents distinguishes it from the xylenes. It yields benzoic acid, just as toluene does. In this case, as in that of toluene, the paraffin radical is converted into carboxyl. It has been found that no matter what this radical may be, it is, under the same circumstances, converted into carboxyl. Thus, the conversions indicated below take place: —

$$\begin{array}{lcl}
C_6H_5.CH_3 & \text{gives} & C_6H_5.CO_2H. \\
C_6H_5.C_2H_5 & \text{"} & C_6H_5.CO_2H. \\
C_6H_5.C_3H_7 & \text{"} & C_6H_5.CO_2H. \\
C_6H_5.C_5H_{11} & \text{"} & C_6H_5.CO_2H.
\end{array}$$



$$\begin{array}{lcl}
C_6H_4<\genfrac{}{}{0pt}{}{CH_3}{C_2H_5} & \text{"} & C_6H_4<\genfrac{}{}{0pt}{}{CO_2H}{CO_2H}. \\
C_6H_4<\genfrac{}{}{0pt}{}{CH_3}{C_3H_7} & \text{"} & C_6H_4<\genfrac{}{}{0pt}{}{CO_2H}{CO_2H}, \text{ etc., etc.}
\end{array}$$

**Mesitylene, $C_9H_{12}[=C_6H_3(CH_3)_3]$.** — Mesitylene is contained in small quantity in light oil, and may be obtained in pure condition from this source. It is most readily prepared by treating acetone with sulphuric acid: —

$$3\,C_3H_6O = C_9H_{12} + 3\,H_2O.$$

It is a liquid resembling the lower members of the series in its general properties. It boils at 163°.

Its conduct towards oxidizing agents shows that it is a *trimethyl-benzene.* When boiled with dilute nitric acid, it yields *mesitylenic acid*, $C_9H_{10}O_2$, and *uvitic acid*, $C_9H_8O_4$; and, by further oxidation with chromic acid, *trimesitic acid*, $C_9H_6O_6$, is formed. By distillation with lime, mesitylenic acid yields meta-xylene and carbon dioxide; uvitic acid yields toluene and carbon dioxide; and *trimesitic acid* yields benzene and carbon dioxide. The formation and decomposition of the acids may be represented by the equations following: —

$$\underset{\text{Mesitylene.}}{C_6H_3(CH_3)_3} + 3\,O = \underset{\text{Mesitylenic acid.}}{C_6H_3\left\{\begin{array}{l}CH_3\\CH_3\\CO_2H\end{array}\right.} + H_2O;$$

$$\underset{\text{Mesitylenic acid.}}{C_6H_3\left\{\begin{array}{l}CH_3\\CH_3\\CO_2H\end{array}\right.} + 3\,O = \underset{\text{Uvitic acid.}}{C_6H_3\left\{\begin{array}{l}CH_3\\CO_2H\\CO_2H\end{array}\right.} + H_2O;$$

$$\underset{\text{Uvitic acid.}}{C_6H_3\left\{\begin{array}{l}CH_3\\CO_2H\\CO_2H\end{array}\right.} + 3\,O = \underset{\text{Trimesitic acid.}}{C_6H_3\left\{\begin{array}{l}CO_2H\\CO_2H\\CO_2H\end{array}\right.} + H_2O;$$

$$\underset{\text{Mesitylenic acid.}}{C_6H_3\left\{\begin{array}{l}CH_3\\CH_3\\CO_2H\end{array}\right.} = \underset{\text{Meta-xylene.}}{C_6H_4\left\{\begin{array}{l}CH_3\\CH_3\end{array}\right.} + CO_2;$$

$$\underset{\text{Uvitic acid.}}{C_6H_3\left\{\begin{array}{l}CH_3\\CO_2H\\CO_2H\end{array}\right.} = \underset{\text{Toluene.}}{C_6H_5.CH_3} + 2\,CO_2;$$

$$\underset{\text{Trimesitic acid.}}{C_6H_3\left\{\begin{array}{l}CO_2H\\CO_2H\\CO_2H\end{array}\right.} = \underset{\text{Benzene.}}{C_6H_6} + 3\,CO_2.$$

These transformations show clearly that mesitylene is trimethyl-benzene, but they do not show in what relation the methyl groups stand to each other.

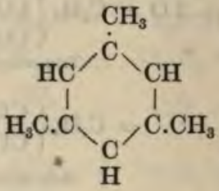
An ingenious speculation in regard to this relation is based upon the fact that mesitylene is formed from acetone. It appears probable that each of the three molecules of acetone taking part in the reaction,

$$3\,C_3H_6O = C_9H_{12} + 3\,H_2O,$$

undergoes the same change. As the product contains three methyl groups, the simplest assumption that can be made is that each acetone molecule gives up water as represented thus:—

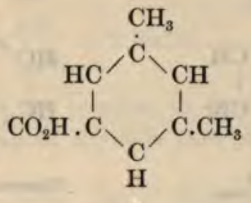
$$\underset{\text{Acetone.}}{CH_3-CO-CH_3} = CH_3-C-CH + H_2O.$$

We thus have three residues, $CH_3-C-CH$, and these unite to form trimethyl benzene. The only way in which the union can be represented, assuming that all three act in the same way, is this:—



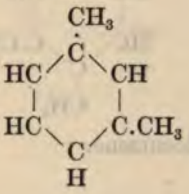
According to this reasoning, mesitylene is a symmetrical compound,—that is to say, each of the three methyl groups bears the same relation to the molecule; and the same is true of each of the three benzene-hydrogen atoms.

This view has been tested by replacing the three hydrogen atoms successively by bromine; and it has been found that the view is confirmed, as but one mono-bromine substitution-product of mesitylene has ever been obtained. Accepting the formula above given for mesitylene, an important conclusion follows regarding the nature of meta-xylene. For we have seen that, by oxidizing mesitylene, we get, as the first product, mesitylenic acid,—which is mesitylene, one of whose methyls has been converted into carboxyl. As all the methyl groups bear the same relation to the molecule, it makes no difference which one is oxidized. The acid has the formula



Now, by distilling this acid with lime, carbon dioxide is given off, and meta-xylene is produced.

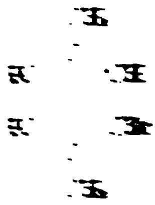
As the change consists in removing the carboxyl, and replacing it by hydrogen, it follows that meta-xylene must be represented by the formula



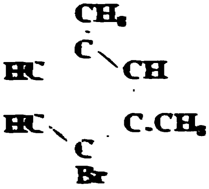
and consequently that, in all meta compounds, the two substituting atoms or groups bear to each other the relation which the two methyl groups bear to each other in this formula for meta-xylene.

**Pseudocumene,** $C_9H_{12}[=C_6H_3(CH_3)_3]$. — This hydrocarbon, which is isomeric with mesitylene, occurs in coal-tar oil, from which it can be made in pure condition. Its properties are similar to those of the lower members of the series. It boils at 169.8°.

Pseudocumene has been made synthetically from brom-para-xylene and methyl iodide, and also from brom-meta-xylene and [illegible] [illegible]. How this is possible will be understood by a [illegible] [illegible] [illegible] [illegible] below:—

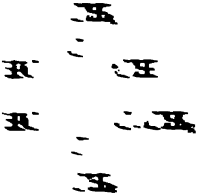


[illegible]



Bromo-meta-xylene.

[illegible] [illegible] [illegible] [illegible] [illegible] in either of the compoun [illegible], [illegible] [illegible] would have the formula



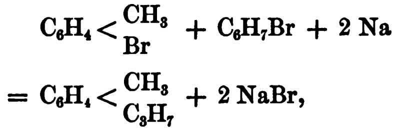
[illegible] Pseudocumene.

[illegible]

$C_{10}H_{14} = C_6H_4 < {}^{CH_3}_{C_3H_7}$

[illegible] [illegible] [illegible] great importance and interest [illegible] [illegible] connection with the well-known gro [illegible] [illegible] group of which camphor and [illegible] [illegible] [illegible] [illegible]. It occurs [illegible] [illegible]. The terpenes, wi [illegible] [illegible] formula $C_{10}H_{16}$ and of which [illegible] [illegible] give up two hydrog [illegible] [illegible]. [illegible] the simplest way is [illegible] [illegible] with phosphorus penta [illegible] [illegible] [illegible]. [illegible] [illegible] boils at 175°.

It has been made synthetically from para-brom-toluene and propyl bromide: —



$$C_6H_4<\begin{matrix}CH_3\\Br\end{matrix} + C_6H_7Br + 2\,Na$$
$$= C_6H_4<\begin{matrix}CH_3\\C_3H_7\end{matrix} + 2\,NaBr,$$

which clearly shows its relation to benzene. As the final product of its oxidation, it yields para-phthalic (terephthalic) acid: —

$$C_6H_4<\begin{matrix}CH_3\\C_3H_7\end{matrix} \text{ gives } C_6H_4<\begin{matrix}CO_2H\\CO_2H\end{matrix};$$

see p. 246.

# CHAPTER XV.

## DERIVATIVES OF THE HYDROCARBONS, $C_nH_{2n-6}$, OF THE BENZENE SERIES.

RECALLING what we learned under the head of Derivatives of the Paraffins, we naturally look for representatives of all the classes of compounds there met with. The derivatives of the paraffins were classified into: —

1. Halogen derivatives.
2. Oxygen derivatives, including the Alcohols, Aldehydes, Acids, etc.
3. Sulphur derivatives, including the Mercaptans, Sulphonic Acids, etc.
4. Nitrogen derivatives, including Cyanides, Amines, Nitro compounds, etc.
5. Metallic derivatives.

The derivatives of the benzene hydrocarbons may be classified in the same way, but a change in the order of consideration will be somewhat more convenient in this connection, owing to many points of analogy which exist between the halogen substitution-products, the nitro compounds, and the sulphonic acids. All of these three classes of derivatives of the benzene hydrocarbons are made by direct treatment of the hydrocarbons with the substituting agents, and in some respects resemble each other, so that they will be considered in connection. As the amido derivatives of this series are made almost exclusively from the nitro compounds by reduction, they will be considered in connection with the nitro compounds; and, further, by treatment of the amido compounds with nitrous acid, a new class of nitrogen derivatives, known as *diazo compounds*, not met with in connection with the paraffins, is formed. These will be considered after the amido compounds.

After these classes have been considered, we shall take up in turn the *oxygen derivatives*, which include the phenols or simple hydroxyl derivatives of the hydrocarbons, the alcohols, aldehydes, acids, and ketones; and, finally, the *hydroxy-acids*, which are strictly analogous to the hydroxy-acids of the paraffin series.

We have thus the following classes: —

1. *Halogen derivatives.*
2. *Nitro compounds.*
3. *Amido compounds.*
4. *Diazo compounds.*
5. *Sulphonic acids.*
6. *Phenols.*
7. *Alcohols.*
8. *Aldehydes.*
9. *Acids.*
10. *Ketones* (and *Quinones*).
11. *Hydroxy-acids.*

The relations of most of these classes to the hydrocarbons are the same as those of the corresponding derivatives of the paraffin series to the paraffins; and the general methods of preparation, as well as the reactions, are the same. Hence, most of the knowledge acquired in the first part of the book may be applied to the series now under consideration.

An enormous number of derivatives of the benzene hydrocarbons have been prepared and studied; but we need study only very few in order to acquire a general knowledge of them. In the following a few of the more important representatives of each class will be studied, mainly with the object of illustrating general facts and general relations.

## Halogen Derivatives of Benzene.

Very little need be said in regard to these derivatives. By direct action of bromine or chlorine upon benzene the hydrogen atoms are replaced one after another, until, as the final products, *hexa-chlor-benzene*, $C_6Cl_6$, and *hexa-brom-benzene*, $C_6Br_6$, are obtained. It has already been stated that, when the action takes place in direct sunlight, addition-products, $C_6H_6Cl_6$ and $C_6H_6Br_6$, are formed. Benzene hexachloride, $C_6H_6Cl_6$, is formed also when chlorine is conducted into boiling benzene. The addition-products are readily decomposed, yielding tri-substitution products of benzene and halogen acid:—

$$C_6H_6Br_6 = C_6H_3Br_3 + 3\,HBr.$$

The substitution-products are very stable. They are, as a rule, formed more easily than the halogen derivatives of the paraffins, and, as a rule, they do not give up the halogens as readily. Thus, while it is possible in the paraffin derivatives to replace chlorine and bromine by hydroxyl, the amido group, etc., these replacements cannot easily be effected in the benzene derivatives. The halogens can be removed by sodium, as shown in the synthesis of hydrocarbons:—

$$C_6H_5Br + CH_3I + 2\,Na$$
$$= C_6H_5.CH_3 + NaBr + NaI, \text{ etc., etc.}$$

They may also be removed by nascent hydrogen, the hydrocarbons being regenerated:—

$$C_6H_4Cl_2 + 4\,H = C_6H_6 + 2\,HCl.$$

This kind of reverse substitution is not, however, effected easily.

Perhaps the best known of the bi-substitution products of the class under consideration is

**Bibrom-benzene,** $C_6H_4Br_2$, which is one of the products of the direct treatment of benzene with bromine. This being a bi-substitution product of benzene, it follows, from what has been said in regard to isomerism in this group, that three isomeric varieties of the substance ought to be obtainable; and the interesting question suggests itself: which one of the three possible bibrom-benzenes is formed by direct treatment of benzene with bromine? The answer to the question is equally interesting. The main product of the action is *para*-bibrom-benzene, while there is always formed in much smaller quantity some of the *ortho* product. The reason why these products are obtained, and not the *meta* compound, is unknown; nor has any plausible hypothesis been suggested to account for the fact.

In studying the substitution-products of benzene, one of the first problems which present themselves is the determination of the relations which the substituting atoms or groups bear to each other. The determination is made, as has been stated, by transforming the compounds into others, the relations of whose groups are known. Thus, to illustrate, when benzene is treated under the proper conditions with bromine, two bibrom-benzenes are formed. Without investigation, we, of course, cannot tell to which series these compounds belong. But, by treating that product which is formed in larger quantity with methyl iodide and sodium, we get *para-xylene*. In other words, by replacing the two bromine atoms of the bibrom-benzene by methyl groups, we get a compound which we know belongs to the para series; and, therefore, we have determined that the bromine product is a *para compound*. In the following the chief reactions made use of for effecting the transformations of the derivatives will be discussed.

## HALOGEN DERIVATIVES OF TOLUENE.

As toluene is made up of a residue of marsh gas, methyl, $CH_3$, and a residue of benzene, phenyl, $C_6H_5$, it might naturally be expected that it would yield two classes of substitution-products: viz., (1) Those in which the substituting atom or group replaces one or more hydrogen atoms of the phenyl group; and (2) those in which the substitution takes place in the methyl. Representatives of both these classes are well known. In general, when *boiling* toluene is treated with chlorine or bromine, products of the second class are obtained; while, when treated in the cold, products of the first class are obtained. Thus, we have the two parallel series of chlorine derivatives: —

| I. | II. |
|---|---|
| $C_6H_4Cl.CH_3$. | $C_6H_5.CH_2Cl$. |
| $C_6H_3Cl_2.CH_3$. | $C_6H_5.CHCl_2$. |
| $C_6H_2Cl_3.CH_3$. | $C_6H_5.CCl_3$. |

When a member of the first class is oxidized, the methyl is changed, and the rest of the compound remains unchanged, as in the case of toluene. Thus, the first substance of class I. yields the product $C_6H_4Cl.CO_2H$; the second, $C_6H_3Cl_2.CO_2H$, etc. These products are *substituted benzoic acids*. On the other hand, all the members of the second class yield the same product that toluene does; viz., *benzoic acid*. Hence, by treatment with oxidizing agents, it is easy to distinguish between the members of the two classes. Further, the halogen atoms contained in the methyl are not as firmly held in combination as those in the phenyl. When, for example, the compound $C_6H_5.CHCl_2$, which is called *benzal chloride*, is treated with water, both chlorine atoms are replaced by oxygen, the product being the aldehyde $C_6H_5.CHO$, which, as we shall see, is the familiar substance, *oil of bitter almonds*. When, however, the isomeric *di-chlor-toluene* $C_6H_3Cl_2.CH_3$ is heated with water, no change takes place.

Regarding those simple substitution-products of toluene which contain one halogen atom in the phenyl, such as mono-brom-toluene, $C_6H_4Br.CH_3$, we see that they are bi-substitution products of benzene, and hence capable of existing in three isomeric varieties, ortho, meta, and para. The products formed by direct treatment of toluene with chlorine or bromine are mixtures consisting mostly of the para compound, together with a much smaller quantity of the ortho compound.

The determination of the series to which one of these products *belongs* may be made by replacing the halogen by methyl, and thus getting the corresponding xylene. The main product of the action of bromine on toluene is thus converted into para-xylene, and is therefore para-brom-toluene.

### HALOGEN DERIVATIVES OF THE HIGHER MEMBERS OF THE BENZENE SERIES.

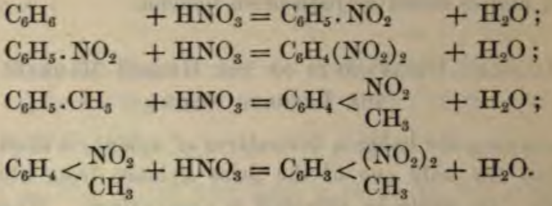
Concerning the halogen derivatives of xylene, it need only be said that the only one of the three xylenes from which pure products can easily be obtained is para-xylene. When this is treated with bromine it yields but one mono-brom-xylene. The significance of this fact has been discussed above. The mono-substitution products obtained from the other xylenes are mixtures which it is very difficult, and in some cases impossible, to separate into their constituents. Mesitylene and pseudocumene, though both are tri-methyl-benzenes, conduct themselves quite differently towards bromine,—the former yielding only one mono-bromine product; the latter, a mixture of several.

### NITRO COMPOUNDS OF BENZENE AND TOLUENE.

In speaking of nitro compounds in connection with the paraffin derivatives (see p. 100), it was stated that they are obtained much more readily from the benzene hydrocarbons than from the paraffins. But few nitro derivatives of the paraffins are known. As will be remembered, they cannot be prepared by treating the paraffins with nitric acid, but must be made by circuitous reactions, the principal one being the treatment of the halogen derivatives with silver nitrite: —

$$C_2H_5Br + AgNO_2 = \underset{\text{Nitro-ethane.}}{C_2H_5(NO_2)} + AgBr.$$

The preparation of a nitro derivative of a hydrocarbon of the benzene series is a simple matter. It is only necessary to bring the hydrocarbon in contact with strong nitric acid, when reaction takes place, and one or more hydrogen atoms of the hydrocarbon are replaced by the nitro group $NO_2$, as illustrated in the equations, —



$$
\begin{aligned}
&C_6H_6 && + HNO_3 = C_6H_5 . NO_2 && + H_2O ;\\
&C_6H_5 . NO_2 && + HNO_3 = C_6H_4(NO_2)_2 && + H_2O ;\\
&C_6H_5 . CH_3 && + HNO_3 = C_6H_4 < {NO_2 \atop CH_3} && + H_2O ;\\
&C_6H_4 < {NO_2 \atop CH_3} && + HNO_3 = C_6H_3 < {(NO_2)_2 \atop CH_3} && + H_2O .
\end{aligned}
$$

The nitro compounds thus obtained are not acids, nor are they ethereal salts of nitrous acid, as the formulas might lead us to suppose. The most rational view held in regard to them is, that they are formed from nitric acid by the replacement of hydroxyl by benzene radicals, as indicated thus: —

$$C_6H_5\boxed{H + HO}.NO_2 = C_6H_5 . NO_2 + H_2O.$$

**Mono-nitro-benzene, $C_6H_5 . NO_2$.** — This substance is made by treating benzene with concentrated nitric acid, or with a mixture of ordinary concentrated nitric and sulphuric acids. In the latter case, the sulphuric acid facilitates the reaction, probably by preventing the dilution of the nitric acid by the water necessarily formed.

**Experiment 58.** Make a mixture of $150^{cc}$ ordinary concentrated sulphuric acid, and $75^{cc}$ ordinary concentrated nitric acid. Let it cool to the ordinary temperature. Put the vessel containing it in water, and add about $15^{cc}$ to $20^{cc}$ benzene, a few drops at a time, waiting each time until the reaction is complete. Shake well until the benzene is dissolved; then pour slowly into about a litre of cold water. A yellow oil will sink to the bottom. This is nitro-benzene. Pour off the acid and water; wash two or three times with water; separate the water by means of a pipette, and dry by adding a little granulated calcium chloride. After standing for some time, pour off from the calcium chloride, and distil from a proper sized distilling-bulb, noting the boiling temperature.

Nitro-benzene is a liquid which boils at 205°, and has the specific gravity 1.2. Its odor is like that of the oil of bitter almonds, and it is hence used in many cases instead of the latter. It is known as the *essence of mirbane*. It is manufactured on the large scale, and used principally in the preparation of aniline.

**Dinitro-benzene, $C_6H_4(NO_2)_2$.** — This is a product of the further action of nitric acid on benzene, or on nitro-benzene.

**Experiment 59.** Make a mixture of $50^{cc}$ concentrated sulphuric acid, and $50^{cc}$ *fuming* nitric acid. Without cooling add *very slowly* about $10^{cc}$ benzene from a pipette with a fine opening. After the action is over, boil the mixture for a short time; then pour into about half a litre of water. Filter off the solid substance thus precipitated, press it between layers of filter-paper, and crystallize from alcohol.

Dinitro-benzene crystallizes in long, fine needles, or thin, rhombic plates. Melting-point, 89.9°.

By means of two reactions, which will be considered under the head of Diazo Compounds, it is a simple matter to replace the two nitro groups by bromine, thus converting dinitro-benzene into bibrom-benzene. When the latter is converted into xylene, the product is meta-xylene. Hence, ordinary dinitro-benzene is a meta compound.

**Nitro-toluenes, $C_6H_4(NO_2).CH_3$.** — When toluene is treated with strong nitric acid, substitution always takes place in the phenyl. The chief mono-nitro-toluene is a para compound; while, at the same time, a little of the isomeric ortho compound is obtained.

NOTE FOR STUDENT. — What mono-bromine products are formed by direct treatment of toluene with bromine? Given a mono-nitro-toluene. How is it possible to determine whether it belongs to the ortho, the meta, or the para series?

By treatment with nascent hydrogen, the nitro-toluenes are converted into the corresponding amido compounds, called *Toluidines* (which see).

### AMIDO COMPOUNDS OF BENZENE, ETC.

The amido derivatives of the paraffins are made, for the most part, by treating the halogen derivatives with ammonia: —

$$C_2H_5Br + NH_3 = C_2H_5 . NH_2 + HBr.$$

In speaking of these derivatives, however, attention was called to the fact that they may also be made by treating nitro compounds with nascent hydrogen. The latter method is one of great importance in the benzene series. It is used exclusively in the preparation of the amido derivatives of the benzene hydrocarbons. Several of these derivatives are well known, the simplest and best known being *amido-benzene* or *aniline*.

**Aniline, $C_6H_7N(= C_6H_5 . NH_2)$.** — Aniline was first obtained from indigo by distillation. *Anil* is the Portuguese and French name of the indigo plant, and it is from this that the name aniline is derived. Aniline is found in coal tar and in bone oil, a product of the distillation of bones. It is prepared by reduction of nitro-benzene with nascent hydrogen. On the large scale the hydrogen is obtained from hydrochloric acid and iron. For laboratory purposes tin and hydrochloric acid are perhaps best. Other reducing agents, such as an ammoniacal solution of ammonium sulphide, hydriodic acid, etc., also effect the change, which is represented by the following equation: —

$$C_6H_5 . NO_2 + 6\,H = C_6H_5 . NH_2 + 2\,H_2O.$$

**Experiment 60.** Dissolve the nitro-benzene obtained in Exp. 58 in alcoholic ammonia, and saturate the solution with hydrogen sulphide, keeping it slightly warm. On the water-bath distil off the excess of ammonium sulphide and some of the alcohol. To the residue add dilute hydrochloric acid. This will dissolve the aniline, but leave any unchanged nitro-benzene undissolved. Separate the latter. Evaporate to dryness; mix with a little lime, and distil from a dry vessel. Aniline will pass over.

*Aniline* is a colorless liquid which rapidly becomes colored in the air. It boils at 184.5°. It solidifies at a low temperature; is easily soluble in alcohol, but slightly soluble in water. The solution in water has only a very slight alkaline reaction.

**Experiment 61.** To an aqueous solution of a little of the aniline obtained in Exp. 60, in a test-tube, add a filtered solution of bleaching powder (calcium hypochlorite). A beautiful purple color is produced.

To a solution of aniline in concentrated sulphuric acid add a few drops of an aqueous solution of potassium bichromate. A blue color is produced.

Aniline bears to benzene the same relation that ethyl-amine or amido-ethane bears to ethane. It is a substituted ammonia, and, like other bodies of the same class, it unites directly with acids, forming salts. Thus, with hydrochloric, nitric, and sulphuric acids the action takes place as represented below: —

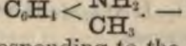
$$\begin{aligned} C_6H_5.NH_2 + HCl &= (C_6H_5.NH_3)Cl; \\ C_6H_5.NH_2 + HNO_3 &= (C_6H_5.NH_3)NO_3; \\ C_6H_5.NH_2 + H_2SO_4 &= C_6H_5.NH_3HSO_4. \end{aligned}$$

The formation of aniline hydrochloride was illustrated in Exp. 60, as was also the decomposition of an aniline salt by a caustic alkali: —

$$2\,(C_6H_5.NH_3)Cl + Ca(OH)_2 = 2\,C_6H_5.NH_2 + 2\,H_2O + CaCl_2.$$

Among the most interesting changes which can be effected in aniline is that which takes place when it is treated with nitrous acid (see Diazo Compounds, below).

Note for Student. — What change is usually effected in amido compounds by treating them with nitrous acid?

**Toluidines, amido-toluenes,**  $C_6H_4{<}\begin{matrix}NH_2\\CH_3\end{matrix}$. — The toluidines, of which there are three corresponding to the three nitro-toluenes, are made from the latter in the same way that aniline is made from nitro-benzene. As *para-nitro-toluene* is the best known of the three nitro-toluenes, so *para-toluidine* is the best known of the three toluidines.

The properties of the toluidines are much like those of aniline.

Treated with various oxidizing agents, a mixture of aniline and the toluidines is converted into a compound known as *rosaniline*. This is the mother substance of the large group of bodies known as the *aniline dyes*. Rosaniline and its derivatives, the aniline dyes, will be considered under *Tri-phenyl-methane* (which see).

By nitrous acid the toluidines are transformed in the same way that aniline is (see Diazo Compounds).

The **xylidines** bear to the three xylenes the same relation that aniline bears to benzene. It is not a simple matter to get any one of them in pure condition.

### DIAZO COMPOUNDS OF BENZENE, ETC.

The usual action of nitrous acid on amido compounds is represented by the equation, —

$$R.NH_2 + HNO_2 = R.OH + H_2O + N_2.$$

When an amido derivative of a hydrocarbon of the benzene series is treated with nitrous acid, and certain precautions are taken, a product is obtained which contains two nitrogen atoms, and which is, therefore, called a *diazo compound*. Thus, in the case of aniline sulphate, the action is represented by the equation, —

$$\underset{\text{Aniline sulphate.}}{C_6H_5NH_2.H_2SO_4} + HNO_2 = \underset{\text{Diazo-benzene sulphate.}}{C_6H_5N_2.HSO_4} + 2\,H_2O.$$

So, also, with the nitrate we have, —

$$\underset{\text{Aniline nitrate.}}{C_6H_5NH_2.HNO_3} + HNO_2 = \underset{\text{Diazo-benzene nitrate.}}{C_6H_5N_2.NO_3} + 2\,H_2O.$$

From these salts the diazo-benzene itself can be set free by means of acetic acid. It has been found to have the formula

$C_6H_5N_2(OH)$. This compound is, however, very unstable, and is at once decomposed.

**Experiment 62.** Arrange an apparatus as shown in Fig. 14. In flask *A* put some coarsely-powdered arsenic trioxide (about 50$^g$), and through the funnel-tube pour 40$^{cc}$ to 50$^{cc}$ ordinary nitric acid of specific gravity 1.35. *B* is an empty cylinder surrounded by water. *C* and *D* are small flasks of about 50$^{cc}$ capacity, in each of which should be brought 10$^g$ aniline nitrate, and 12$^{cc}$ ice-cold water.

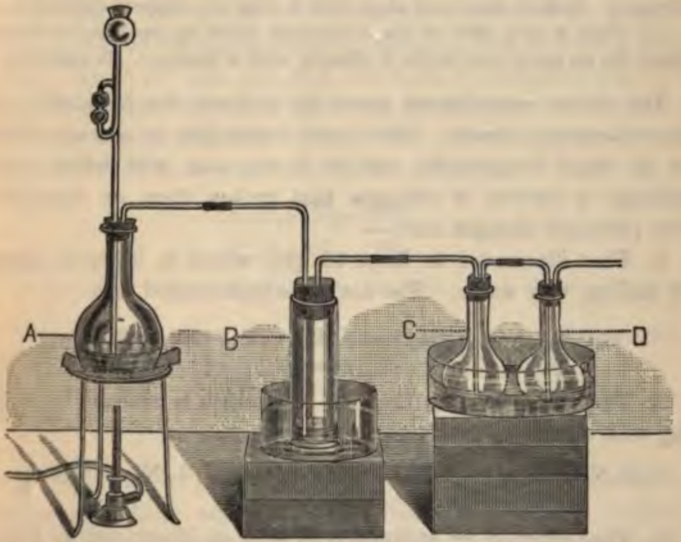


Fig. 14.

They are kept in *ice water*. Pass a current of the oxides of nitrogen until the material in the flasks dissolves. Add to the solution about an equal volume of alcohol previously cooled to 0°, and then a little cold ether. If the operation has been carried out properly, a copious precipitate of crystals of *diazo-benzene nitrate* is formed. Filter off with the aid of a suction-pump, and, *without delay*, proceed to study the properties of the compound.

(*a*) Dissolve a little in water of the ordinary temperature, and allow the solution to stand. Decomposition, indicated by change of color, will take place.

(*b*) Boil a little with water in a test-tube, and notice the odor of phenol or carbolic acid.

(*c*) Boil a few grams with alcohol in a test-tube, and notice the odor of aldehyde. Add water, and notice the light, colorless oil at the top of the liquid, which has the odor of benzene.

(*d*) Boil some with hydrochloric acid. Chlor-benzene is formed, which sinks to the bottom when water is added.

In all these experiments a gas is evolved which can be shown to be nitrogen. Collect some, and show that it does not support combustion.

(*e*) Place a very little of the compound, dried by pressing in filter-paper, on an anvil, and strike it sharply with a hammer. It explodes.

The above experiments serve to indicate the instability of diazo-benzene nitrate. This same instability is characteristic of all diazo compounds, and it is the ease with which they undergo a variety of changes that makes them so valuable. The principal changes are: —

1. That illustrated in Exp. 62 (*b*), which is brought about by boiling with water. The action is represented thus: —

$$C_6H_5N_2.NO_3 + H_2O = \underset{\text{Phenol.}}{C_6H_5.OH} + N_2 + HNO_3.$$

2. That illustrated in Exp. 62 (*c*), which is effected by boiling with alcohol: —

$$C_6H_5N_2.NO_3 + C_2H_6O = \underset{\text{Benzene.}}{C_6H_6} + C_2H_4O + N_2 + HNO_3.$$

3. That effected by hydrochloric acid as illustrated in Exp. 62 (*d*): —

$$C_6H_5N_2.NO_3 + HCl = \underset{\text{Mono-chlor-benzene.}}{C_6H_5Cl} + N_2 + HNO_3.$$

Changes similar to the last are effected by hydrobromic and hydriodic acids, the chief products being brom-benzene and iodo-benzene respectively.

From the above it follows that, if we have a compound containing a nitro group, we can, by making the diazo compound, transform it (1) into the corresponding hydroxyl derivative; (2) into the corresponding chlorine, bromine, or iodine derivative; or, (3) we can eliminate the nitro group, and replace it by hydrogen. These reactions involving the use of the diazo compounds have been used very extensively in the investigation of the substitution-products of the benzene series.

NOTE FOR STUDENT. — How can the relation of the groups in dinitro-benzene be determined by using the diazo reactions?

As regards the relation of diazo-benzene to benzene, it seems clear, from the reactions above considered, that in it the phenyl group $C_6H_5$ is present, and that this is in combination with two nitrogen atoms. In the compounds, the two atoms of nitrogen form the connecting link between the phenyl group and the other constituent, as expressed in the formulas

$$C_6H_5-N_2-NO_3,$$
$$C_6H_5-N_2-OK,$$
$$C_6H_5-N_2-Br, \text{ etc.}$$

The decompositions all indicate the correctness of this view. How the nitrogen atoms are united, we do not know.

## SULPHONIC ACIDS OF BENZENE, ETC.

The methods of preparation of the sulphonic acids, and the relations of these acids to the hydrocarbons, were considered pretty fully, in connection with the paraffins. Three general methods for their preparation were given. These are: —

1. Oxidation of the mercaptans; thus, ethyl-sulphonic acid is formed by oxidation of ethyl-mercaptan, —

$$C_2H_5.SH + 3\,O = C_2H_5.SO_3H.$$

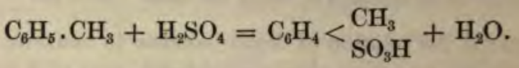
2. Treatment of a halogen substitution-product with a sulphite, —

$$C_2H_5Br + Na_2SO_3 = C_2H_5.SO_3Na + NaBr.$$

3. Treatment of a hydrocarbon with sulphuric acid. This method is not applicable to the paraffins, but is the one used almost exclusively in the case of the benzene hydrocarbons. Benzene-sulphonic acid is formed thus: —

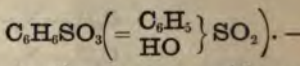
$$C_6H_6 + H_2SO_4 = C_6H_5.SO_3H + H_2O.$$

Toluene-sulphonic acid is formed thus: —



$$C_6H_5.CH_3 + H_2SO_4 = C_6H_4<\begin{matrix}CH_3\\SO_3H\end{matrix} + H_2O.$$

The reasons for regarding the sulphonic acids as sulphuric acid in which hydroxyl is replaced by radicals, were given on p. 76; and the student is advised to re-read carefully what is there said.



**Benzene-sulphonic acid, $C_6H_6SO_3\left(=\left.\begin{matrix}C_6H_5\\HO\end{matrix}\right\}SO_2\right)$.** — This acid is made most readily by treating benzene with ordinary concentrated sulphuric acid.

**Experiment 63.** In a flask bring together about $50^{cc}$ benzene and $100^{cc}$ concentrated sulphuric acid (ordinary). Connect with an inverted condenser (see Fig. 8, p. 70), and boil for several hours, until the greater part of the benzene has passed into solution. Pour the contents of the flask into a large evaporating dish of at least $8^l$ to $10^l$ capacity, containing $4^l$ to $5^l$ water. Heat gently, and add gradually, stirring meanwhile, *finely-powdered* chalk, until the solution has become neutral. Pass through a muslin filter attached to a wooden frame, and wash thoroughly with hot water. Afterwards refilter the filtrate through a paper filter. Evaporate to quite a small volume (say $500^{cc}$ to $700^{cc}$), and filter from gypsum. In solution there is now the calcium salt of the sulphonic acid. Add just enough of a solution of potassium carbonate to precipitate exactly the calcium; filter off from the calcium carbonate, and evaporate to dryness, finally, on the water-bath. To prevent caking it is necessary to stir the thick, syrupy mass. When it is nearly dry, it is best to powder it, and complete the drying at 100° to 120° in an air-bath. The potassium salt may be used for a number of *experiments.*

**Experiment 64.** In a dry evaporating dish mix $15^{g}$ to $20^{g}$ potassium benzene-sulphonate and an equal weight of phosphorus pentachloride, by means of a dry pestle. The mass becomes semi-liquid and hot, and hydrochloric acid is given off, in consequence of the action of the moisture of the air on the chlorides of phosphorus. Hence, the experiment should be performed under a hood or out of doors. The reaction which takes place is represented by the equation, —

$$C_6H_5 . SO_2OK + PCl_5 = C_6H_5 . SO_2Cl + POCl_3 + KCl.$$

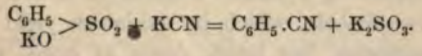
After the action is over, and the mass cooled down to the ordinary temperature, add about a litre of cold water. Everything will dissolve except the sulphon-chloride, $C_6H_5 . SO_2Cl$, which will remain as a heavy oil at the bottom of the vessel. Pour off the greater part of the water, and add $30^{g}$ to $40^{g}$ solid ammonium carbonate. The chloride is thus converted into the corresponding sulphon-amide, thus: —

$$C_6H_5 . SO_2Cl + 2\,NH_3 = C_6H_5 . SO_2NH_2 + NH_4Cl.$$

After cooling, filter off the sulphon-amide; wash well with cold water, and crystallize from water. The product crystallizes in needles, fusing at 153°.

NOTE FOR STUDENT. — Refer back to what was said regarding the acid chlorides and acid amides, paying particular attention to the general methods of preparation and their decompositions.

**Experiment 65.** Mix $20^{g}$ potassium cyanide with an equal weight of dry potassium benzene-sulphonate, and distil from a small retort. The distillate is impure phenyl cyanide, $C_6H_5.CN$: —



$$\begin{matrix} C_6H_5 \\ KO \end{matrix}\!\!>SO_2 + KCN = C_6H_5.CN + K_2SO_3.$$

Put the phenyl cyanide in a flask of $600^{cc}$ to $700^{cc}$ capacity, and add $300^{cc}$ of a moderately strong solution of potassium hydroxide in water. Connect with an inverted condenser, and boil for two or three hours. What is given off? Test with the nose the gases at the upper end of the condenser-tube. After cooling, dilute with about an equal volume of water, and acidify with hydrochloric acid. A solid substance is precipitated. Filter off, wash, and crystallize from water. It is benzoic acid. The reaction with caustic potash is represented thus: —

$$C_6H_5.CN + H_2O + KOH = C_6H_5.CO_2K + NH_3.$$

Benzene-sulphonic acid itself is a very easily soluble substance. It is a strong acid, and yields a series of salts and other derivatives.

When fused with potassium hydroxide, benzene-sulphonic acid is converted into phenol (Exp. 66, p. 270):—

$$C_6H_5.SO_3K + KOH = C_6H_5.OH + K_2SO_3.$$

By further treatment of benzene with fuming sulphuric acid a benzene-disulphonic acid is formed. This is capable of the same transformations as the mono-sulphonic acid.

NOTE FOR STUDENT.—By what reaction could benzene-disulphonic acid be transformed into the corresponding dicarbonic acid, $C_6H_4(CO_2H)_2$? Suppose the product obtained were meta-phthalic acid, what conclusion could be drawn with reference to the relation of the two sulpho groups, $SO_3H$, in the disulphonic acid?

### PHENOLS, OR HYDROXYL DERIVATIVES OF BENZENE, ETC.

The hydroxyl derivatives of the paraffins are called *alcohols*. As will be remembered they are of three kinds, each of which is characterized by certain properties. We have:—

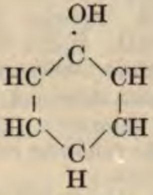
1. *Primary alcohols* of which ordinary ethyl alcohol is the commonest example, and which, when oxidized, yield aldehydes and then acids containing the same number of carbon atoms.

2. *Secondary alcohols*, which by oxidation yield acetones and then acids containing a smaller number of carbon atoms.

3. *Tertiary alcohols*, which by oxidation yield neither aldehydes nor acetones, but break down at once, yielding acids with a smaller number of carbon atoms.

The primary alcohols were shown to correspond to the formula $C\left\{\begin{matrix}R\\H\\H\\HO\end{matrix}\right.$; the secondary to $C\left\{\begin{matrix}R\\R\\H\\HO\end{matrix}\right.$; and the tertiary to $C\left\{\begin{matrix}R\\R\\R\\HO\end{matrix}\right.$; or, in other words, the primary alcohols contain the group $CH_2.OH$; the secondary, the group $CH.OH$; and the *tertiary*, the group $C.OH$.

Now, the simplest hydroxyl derivative of the members of the benzene series is phenol, $C_6H_5.OH$, or benzene in which one hydrogen is replaced by hydroxyl. Representing this compound in terms of the accepted benzene hypothesis, we have the formula



According to this, phenol appears to be allied to the tertiary alcohols, as it contains the group C.OH, and not $CH_2OH$ nor CH.OH. We shall see that, in fact, phenol conducts itself towards oxidizing agents like the tertiary alcohols.

All compounds which contain hydroxyl in the place of the benzene-hydrogen atoms of benzene and its homologues are called *phenols*. As in the case of alcohols, there are phenols containing one hydroxyl, or *mon-acid phenols;* those containing two hydroxyls, or *di-acid phenols;* those containing three hydroxyls, or *tri-acid phenols*, etc. Some of these are familiar substances.

### MON-ACID PHENOLS.

**Phenol, carbolic acid, $C_6H_6O(=C_6H_5OH)$.** — Phenol is found in nature in small quantities in the urine. It is formed by the distillation of wood, coal, and bones. Hence, it is a constituent of coal tar, and from this it is prepared. For this purpose the *heavy oil* (see p. 231) is treated with an alkali which dissolves the phenol. From the solution it is precipitated by hydrochloric acid. It is purified by distillation.

Phenol may also be made by converting nitro-benzene into aniline; then into diazo-benzene, and boiling this with water (see Exp. 62 (*b*)); and by melting benzene-sulphonic acid with potassium hydroxide.

**Experiment 66.** In a silver (or iron) crucible, or evaporating dish, melt $40^g$ to $50^g$ potassium hydroxide, after adding a few cubic centimetres of water. Now add gradually $10^g$ finely-powdered potassium benzene-sulphonate, obtained in Exp. 63, stirring constantly with a silver (or iron) spatula. Do not heat to a very high temperature. After the mass has been kept in a state of fusion for one-quarter to one-half an hour, let it cool. Dissolve in $200^{cc}$ to $250^{cc}$ water, and acidify with hydrochloric acid. Notice the odor of the gases given off. What gas do you detect? When the liquid has cooled down, extract with ether in a glass-stoppered cylinder. From the ether extract distil the ether on a water-bath. The residue is impure phenol, which may be detected by the following reactions, for which a solution in water should be prepared:—

(*a*) A few drops of ferric chloride solution gives a beautiful violet color.

(*b*) Add one-fourth volume of ammonia, and then a few drops of a dilute solution of bleaching powder. A blue color is produced.

(*c*) Bromine water gives a yellowish-white precipitate of tri-brom-phenol.

The reaction which takes place in melting potassium hydroxide and potassium benzene-sulphonate together is represented by the equation,—

$$C_6H_5.SO_3K + KOH = C_6H_5.OH + K_2SO_3.$$

It effects the replacement of the sulpho group, $SO_3H$, by hydroxyl.

Phenol, when pure, crystallizes in beautiful colorless rhombic needles. The presence of a little water prevents it from solidifying. It has a peculiar, penetrating odor; boils at 180°; is difficultly soluble in water (1 part in 15 parts water at ordinary temperature); mixes with alcohol and ether in all proportions; and is poisonous.

Phenol forms compounds with several metals. Among these may be mentioned the following:—

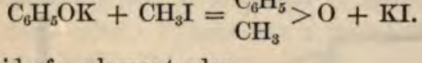
*Potassium phenolate*, $C_6H_5.OK$, made by dissolving potassium in phenol, and by treating phenol with caustic potash.

*Barium phenolate*, $(C_6H_5O)_2Ba + 2\,H_2O$, made by dissolving phenol in baryta water.

*Lead oxide phenol*, $C_6H_6O.PbO$, made by dissolving lead oxide in phenol.

It also forms ethers, of which the methyl and diphenyl ethers may serve as examples: —

**Methyl-phenyl ether,** $C_7H_8O\left(=\begin{matrix}C_6H_5\\CH_3\end{matrix}>O\right)$. — This substance, also called *anisol*, is obtained from anisic acid and from oil of winter-green by boiling with baryta water. It is made also by treating potassium phenolate, $C_6H_5OK$, with methyl iodide: —



$$C_6H_5OK + CH_3I = \begin{matrix}C_6H_5\\CH_3\end{matrix}>O + KI.$$

It is a liquid of a pleasant odor.

Note for Student. — Compare this substance with *ordinary ether*. What method analogous to that above mentioned may be used in the preparation of ordinary ether?

**Diphenyl ether,** $C_{12}H_{10}O\left(=\begin{matrix}C_6H_5\\C_6H_5\end{matrix}>O\right)$. — This bears to phenol the same relation that ordinary ether bears to alcohol.

With acids, phenol, like the alcohols, yields ethereal salts in which the phenyl group, $C_6H_5$, takes the place of a metal. Among the compounds of this class which phenol forms with organic acids, the following may be mentioned: —

**Phenyl acetate,** $C_8H_8O_2(=CH_3.CO_2.C_6H_5)$. — This is formed by treating phenol with acetyl chloride.

Note for Student. — What use is acetyl chloride put to as a reagent in organic chemistry? Explain its use. What conclusion may be drawn from the fact that acetyl chloride acts upon phenol, replacing one hydrogen by acetyl, $C_2H_3O$?

*Substitution-products of phenol.* Phenol is very susceptible to the action of various reagents, and a large number of substitution-products have been made from it.

The ease with which bromine acts upon it was illustrated in

Exp. 66 (*c*). It was shown that, by the addition of bromine water to the water solution of phenol, tri-brom-phenol is formed.

Dilute nitric acid acts upon phenol, yielding two mono-nitro-phenols, $C_6H_4\left\{\begin{matrix}NO_2\\ OH\end{matrix}\right.$, one of which has been shown to belong to the ortho series, the other to the para series.

**Experiment 67.** Add $20^g$ phenol to a mixture of $80^{cc}$ water and $40^{cc}$ ordinary concentrated nitric acid (sp. gr. 1.34). Stir, and, after a time, pour off the dilute acid from the oil. Wash with water, and then put it into a flask, with about a litre of water, arranged as shown in Fig. 15. Flask *A* holds nothing but water; while the oil, together with water, are in *B*. From *A* a current of steam is passed into *B*, which is heated by means of a lamp. Yellow crystals pass over and appear in the receiver, while a non-volatile substance remains behind in flask *B*. The volatile substance is ortho-nitro-phenol; the non-volatile is para-nitro-phenol.

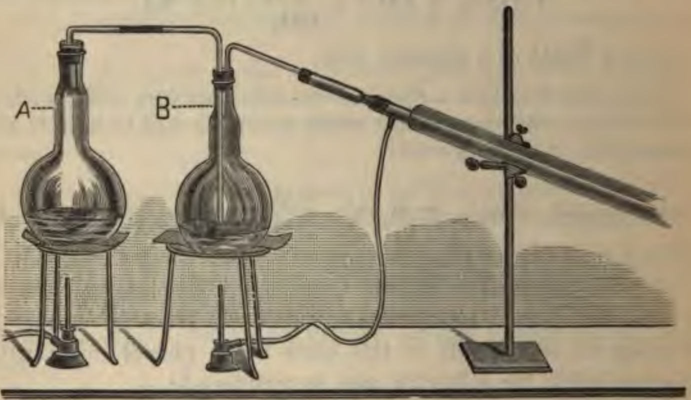


Fig. 15.

**Tri-nitro-phenol, picric acid, $C_6H_3N_3O_7\left(=C_6H_2\left\{\begin{matrix}(NO_2)_3\\ OH\end{matrix}\right.\right)$.** This is formed very easily by the action of strong nitric acid on phenol.

**Experiment 68.** Dissolve $10^g$ to $15^g$ phenol in weak nitric acid, *and to this* solution slowly add some strong nitric acid. Afterward dilute with water; filter off the picric acid, and wash. Dissolve in dilute potassium carbonate solution, and evaporate to crystallization.

Picric acid forms yellow crystals, has a very bitter taste, is poisonous, decomposes with explosion when heated rapidly. It dyes wool and silk yellow.

Note for Student. — Is there any analogy between tri-nitro-phenol and tri-nitro-glycerin? What is the essential difference between them?

One of the most interesting properties of tri-nitro-phenol is its power to form salts. It acts like a strong acid. It will thus be seen, that, while the substance $C_6H_5.OH$ has only very slight acid properties, the same substance, with three of its hydrogens replaced by nitro groups, $C_6H_2(NO_2)_3.OH$, has strong acid properties. In the salts, which have the general formula $C_6H_2(NO_2)_3.OM$, the metals replace the hydrogen of the hydroxyl. Among them may be mentioned the potassium salt which was obtained in Exp. 68; this explodes when heated and when struck. *Ammonium picrate*, $C_6H_2(NO_2)_3.ONH_4$, is used as a constituent of explosives.

**Phenyl mercaptan, Phenyl hydrosulphide,** $\Big\}$ $C_6H_6S(= C_6H_5.SH)$. — This bears the same relation to phenol that mercaptan bears to alcohol. It may be made by reducing benzene-sulphonic acid. This reduction is effected by first making the sulphon-chloride, $C_6H_5.SO_2Cl$, (Exp. 64), and then treating this with nascent hydrogen.

Note for Student. — What is the effect of oxidizing the mercaptans?

It may be made, also, by treating phenol with phosphorus pentasulphide, the effect of this reagent being to replace oxygen by sulphur.

Note for Student. — What analogy is there between the action of phosphorus pentachloride and of phosphorus pentasulphide on compounds containing oxygen?

Phenyl mercaptan is a liquid, with a very disagreeable odor. With *mercuric oxide* it forms a crystallized compound, $(C_6H_5S)_2Hg$.

**Cresols,** $C_7H_8O\left(=C_6H_4<\begin{matrix}CH_3\\OH\end{matrix}\right)$. — There are three cresols, or hydroxyl derivatives of toluene, of the formula $C_6H_4<\begin{matrix}CH_3\\OH\end{matrix}$. They are all found in coal tar, and the tars from pine and beech wood. When mixed together, it is difficult to separate them. To obtain them in pure condition, it is therefore best to make them from the three toluidines, or from the three sulphonic acids of toluene.

Note for Student. — Give the equations representing the reactions involved in passing from the three toluidines to the cresols, and from the three toluene-sulphonic acids to the cresols.

The cresols resemble phenol very closely.

**Creosote** is a mixture of chemical compounds contained in wood tar. It contains the cresols. Coal-tar creosote consists largely of phenol.

**Thymol, propyl-meta-cresol,** $C_{10}H_{14}O\left(=C_6H_3\left\{\begin{matrix}CH_3\\OH\ (m)\\C_3H_7(p)\end{matrix}\right.\right)$.[1] This phenol is contained in oil of thyme, together with cymene. It forms large monoclinic crystals, which melt at 50°. It has a pleasant odor, like that of the oil of thyme. Treated with phosphorus pentoxide, it yields meta-cresol; while, when treated with phosphorus pentasulphide, it yields cymene. These two reactions indicate that the groups contained in thymol bear to each other the relations indicated by the formula given above. It is one of the two theoretically possible hydroxyl derivatives. The other one, *carvacrol*, has the hydroxyl in the ortho position relatively to methyl. It has been made from the corresponding cymene-sulphonic acid; is found in nature in the ethereal oil of *Origanum hirtum;* and may be made from carvol, or the oil of caraway.

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[1] Formulas of this kind serve very well to indicate the relations of the groups and atoms contained in benzene derivatives. This one, for example, indicates that the hydroxyl is in the meta position $(m)$ to methyl; while the propyl is in the para position to methyl $(p)$. For bi-substitution products, such formulas may also be used. Thus, the three toluidines may be represented by $C_6H_4<\begin{matrix}CH_3\\NH_{2(o)}\end{matrix}$, $C_6H_4<\begin{matrix}CH_3\\NH_{2(m)}\end{matrix}$, and $C_6H_4<\begin{matrix}CH_3\\NH_{2(p)}\end{matrix}$.

## DI-ACID PHENOLS.

The three theoretically possible di-hydroxyl benzenes, $C_6H_4<^{OH}_{OH}$, are all well known.

**Pyrocatechin,**
**Ortho-di-hydroxy-benzene,** $\Big\} C_6H_6O_2\left(= C_6H_4 < {OH \atop OH_{(o)}}\right)$.

This substance is a frequent product of the dry distillation of natural substances, — as of catechu, morintannic acid, etc., — and of the melting of resins with caustic potash. It may be made by melting ortho-iodo-phenol or ortho-phenol-sulphonic acid with caustic potash. It forms crystals, which melt at 104°. It is easily soluble in water, alcohol, and ether.

The dilute solution in water gives with ferric chloride a dark-green color, which becomes violet on the addition of a little sodium carbonate.

**Resorcin,**
**Meta-di-hydroxy-benzene,** $\Big\} C_6H_6O_2\left(= C_6H_4 < {OH \atop OH_{(m)}}\right)$.

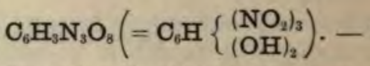
Resorcin is formed by the melting of a number of resins with caustic potash, as of galbanum, sagapenum, asafœtida, etc. It is made, also, by melting meta-iodo-phenol or meta-benzene-disulphonic acid with caustic potash.

It crystallizes from water, usually in thick rhombic prisms. Melting-point, 110°.

With ferric chloride, the water solution gives a dark purple color. Heated for a few minutes with phthalic acid in a test-tube, a yellowish-red mass is formed. When this is added to dilute caustic soda, a wonderfully fluorescent solution is obtained. The explanation of this reaction will be given under the head of Tri-phenyl-methane, when the phthaleins will be considered.

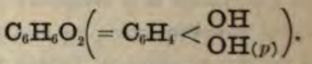
Resorcin is used largely in the manufacture of certain dyes, and is therefore manufactured on the large scale.

**Tri-nitro-resorcin,**
**Styphnic acid,**



$\left.\right\} C_6H_3N_3O_8\left(= C_6H\left\{\begin{matrix}(NO_2)_3\\(OH)_2\end{matrix}\right.\right)$. — This compound is formed by the action of nitric acid on resorcin, and on those resins which give resorcin when treated with caustic potash. It closely resembles picric acid. Heated with bromine and acetic acid, it yields the substance known as *brompicrin*, which has the formula $C(NO_2)Br_3$.

**Hydroquinone,**
**Para-di-hydroxy-benzene,**



$\left.\right\} C_6H_6O_2\left(= C_6H_4 < \begin{matrix}OH\\OH_{(p)}\end{matrix}\right)$.

Hydroquinone is formed by the dry distillation of quinic acid, by reduction of quinone (which see), by the action of chromic acid on aniline, by melting para-iodo-phenol, etc.

It is a crystallized substance which melts at 169°; easily soluble in alcohol, ether, and hot water.

Oxidizing agents, such as ferric chloride, chlorine, etc., convert it into quinone.

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It would lead us too far to consider here the reactions which have been made use of for the purpose of determining to which series each of the three di-hydroxy-benzenes belongs. The principle involved, however, is simple. Either these substances must be converted, directly or indirectly, into others, in regard to the relation of whose groups we have evidence; or substances, the relation of whose groups is known, must be converted into the di-hydroxy-benzenes. The reactions made use of for effecting the conversions are mainly those which have already been considered; viz., the formation of amido compounds from nitro compounds by reduction; the formation of diazo compounds from amido compounds; the formation of (1) hydroxyl derivatives, (2) chlorine, bromine, or iodine derivatives, from the diazo compounds; and the formation of hydroxyl derivatives from sulphonic acids.

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**Orcin, Di-hydroxy-toluene,** $C_7H_8O_2\left(= C_6H_3\left\{\begin{matrix}CH_3\\(OH)_2\end{matrix}\right.\right)$. — There are three dye-stuffs, known as *archil*, *cudbear*, and *litmus*, which are made from different lichens by exposing them in powdered condition in ammoniacal solution to the action of air. They are treated with decomposing urine, from which the ammonia is obtained. *Archil* contains a substance called *orcein*, which may be made from orcin by treating it with ammonia. Orcin is contained in several lichens. It is formed, also, by melting aloes with caustic potash, and by melting chlor-toluene-sulphonic acid with caustic potash. The last reaction shows that orcin is a di-hydroxy-toluene.

Orcin crystallizes in large, colorless, monoclinic prisms. Turns red in the air. Ferric chloride turns the aqueous solution deep violet.

Treated with ammonia in moist air, it is converted into *orcein*, $C_7H_7NO_3$, a substance which dissolves in alkalies, forming beautiful red solutions.

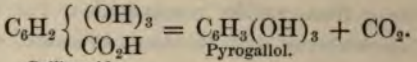
Orcin is manufactured on the large scale, and then converted into orcein, which is used as a dye.

## TRI-ACID PHENOLS.

**Pyrogallol, pyrogallic acid, Tri-hydroxy-benzene,** $C_6H_6O_3[= C_6H_3(OH)_3]$.

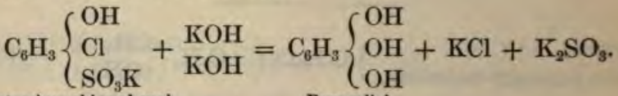
Pyrogallic acid is formed by dry distillation of gallic acid, the reaction being analogous to that by which benzene is produced by distillation of benzoic acid:—

$$\underset{\text{Benzoic acid.}}{C_6H_5.CO_2H} = \underset{\text{Benzene.}}{C_6H_6} + CO_2;$$



$$\underset{\text{Gallic acid.}}{C_6H_2\left\{\begin{matrix}(OH)_3\\CO_2H\end{matrix}\right.} = \underset{\text{Pyrogallol.}}{C_6H_3(OH)_3} + CO_2.$$

It is formed also when one of the chlor-phenol-sulphonic acids is melted with caustic potash:—



$$\underset{\text{Potassium chlor-phenol-sulphonate.}}{C_6H_3\left\{\begin{matrix}OH\\Cl\\SO_3K\end{matrix}\right.} + \begin{matrix}KOH\\KOH\end{matrix} = \underset{\text{Pyrogallol.}}{C_6H_3\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.} + KCl + K_2SO_3.$$

It crystallizes in laminæ or needles; melts at 115°; is easily soluble in water, ether, and alcohol. In alkaline solution it absorbs oxygen rapidly and becomes brown. On account of this power to absorb oxygen it is used in gas analysis. It is poisonous.

With a solution containing a ferrous and a ferric salt it gives a blue color.

Most of the phenols give color reactions with ferric chloride, and most of them change color in the air. These changes in color are undoubtedly due to the action of oxygen upon them. Towards oxidizing agents they are all unstable, most of them breaking down readily and yielding as the chief product of oxidation, carbon dioxide. In general, the larger the number of hydroxyl groups contained in a phenol the less stable it is. We shall see that these same statements hold good for the hydroxy-acids of the benzene group, of which gallic acid and salicylic acid are examples.

## ALCOHOLS OF THE BENZENE SERIES.

The phenols are those hydroxyl derivatives of the benzene hydrocarbons, which contain the hydroxyl in the place of *one or more of* the six benzene hydrogens. But just as there are two classes of halogen substitution-products of toluene, in one of which the substitution has taken place in the benzene residue, and in the other in the marsh-gas residue, as indicated in the two formulas, —

$$C_6H_4Cl.CH_3 \quad \text{and} \quad C_6H_5.CH_2Cl,$$

so, also, there are two classes of hydroxyl derivatives: (1) the phenols, and (2) those in which the hydroxyl is in the marsh-gas residue. The simplest example of the second class corresponds to the formula, $C_6H_5.CH_2.OH$. It is isomeric with the cresols, $C_6H_4.OH.CH_3$, and has entirely different properties. While the cresols are the true homologues of phenol, the new substance is really methyl alcohol in which one of the hydrogens of the methyl has been replaced by phenyl, $C_6H_5$. It may be represented by the formula, $C\left\{\begin{array}{l}C_6H_5\\H\\H\\OH\end{array}\right.$, when its analogy to ethyl alcohol, $C\left\{\begin{array}{l}CH_3\\H\\H\\OH\end{array}\right.$, is at once apparent.

**Benzyl alcohol, $C_7H_8O (= C_6H_5.CH_2OH)$.**—Benzyl alcohol or phenyl carbinol is found in nature in the balsams of Peru and Tolu, and in storax. In these substances it is, for the most part, in combination with benzoic or cinnamic acid. It is made by treating the oil of bitter almonds, which is the corresponding aldehyde, with nascent hydrogen: —

$$\underset{\text{Oil of bitter almonds.}}{C_6H_5.CHO} + H_2 = \underset{\text{Benzyl alcohol.}}{C_6H_5.CH_2.OH.}$$

It is also made by replacing the chlorine in benzyl chloride, $C_6H_5.CH_2Cl$, by hydroxyl, just as methyl alcohol is made from methyl chloride by a similar replacement. In the case of benzyl chloride it may be effected even by boiling for a long time with water: —

$$C_6H_5.CH_2Cl + H_2O = C_6H_5.CH_2OH + HCl.$$

Benzyl alcohol is a liquid with a pleasant odor. It boils at 206.5°.

Note for Student. — Notice the great difference between the boiling-point of methyl alcohol and phenyl-methyl alcohol.

Oxidizing agents convert the alcohol, first, into the oil of bitter almonds or benzoic aldehyde, and finally into benzoic acid. The relations between the three substances are like those between any primary alcohol and the corresponding aldehyde and acid, as shown by the formulas, —

| | | |
|---|---|---|
| $C_7H_8O$, | $C_7H_6O$, | $C_7H_6O_2$, |
| or $C_6H_5.CH_2OH$; | or $C_6H_5.CHO$; | or $C_6H_5.CO_2H$. |
| Benzyl alcohol. | Benzoic aldehyde. | Benzoic acid. |

Hydriodic acid converts benzyl alcohol into toluene: —

$$C_6H_5.CH_2OH + 2\,HI = C_6H_5.CH_3 + H_2O + 2\,I.$$

Benzyl alcohol conducts itself, in most respects, like the primary alcohols of the methyl alcohol series. A large number of its derivatives have been made and studied. Among them are *ethereal salts*, of which *benzyl acetate*, $CH_3.CO.OC_7H_7$, and *benzyl nitrate*, $NO_2.OC_7H_7$, may serve as examples; *ethers*, of which the *methyl ether*, $C_6H_5.CH_2.O.CH_3$, and the *phenyl ether*, $C_6H_5.CH_2.OC_6H_5$, are good examples; and *substitution-products*, of which *chlor-benzyl alcohol*, $C_6H_4Cl.CH_2OH$, and *nitro-benzyl alcohol*, $C_6H_4(NO_2).CH_2OH$, are examples.

These substitution-products are not made by direct treatment of the alcohol with the substituting agents, but by starting from the corresponding substituted toluene. Thus, chlor-benzyl alcohol is made from chlor-toluene, $C_6H_4Cl.CH_3$, by first converting this into chlor-benzyl chloride, $C_6H_4Cl.CH_2Cl$, and then replacing the chlorine of the group $CH_2Cl$ by hydroxyl. By oxidation the substituted benzyl alcohols yield the corresponding substituted benzoic acids: —

$$C_6H_4Cl.CH_2OH + O_2 = \underset{\text{Chlor-benzoic acid.}}{C_6H_4Cl.CO_2H} + H_2O.$$

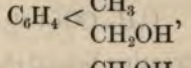
$$C_6H_4(NO_2).CH_2OH + O_2 = \underset{\text{Nitro-benzoic acid.}}{C_6H_4(NO_2)CO_2H} + H_2O.$$

Very few of the alcohols analogous to benzyl alcohol have been prepared. Plainly, the homologues may be of two kinds:

1. Those which are phenyl derivatives of the alcohols of the methyl alcohol series. Of this class, phenyl-ethyl alcohol, $C_6H_5.CH_2.CH_2OH$, the isomeric substance $C_6H_5.CH.OH.CH_3$, and phenyl-propyl alcohol, $C_6H_5.CH_2.CH_2.CH_2OH$, are examples. Phenyl-propyl alcohol is of special interest on account of its connection with cinnamic acid (which see), which has come into prominence since it has been shown to be closely related to the interesting bodies of the indigo group. It occurs in storax in the form of an ethereal salt, which will be spoken of more fully under the head of Cinnamic Acid.

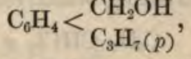
2. Those which are derivatives of xylene, mesitylene, etc., in the same sense as benzyl alcohol is a derivative of toluene. The following belong to this class: —

Tolyl carbinol . . . .



$$C_6H_4 < \begin{matrix} CH_3 \\ CH_2OH \end{matrix},$$

and Cuminyl alcohol . . . .



$$C_6H_4 < \begin{matrix} CH_2OH \\ C_3H_7(p) \end{matrix},$$

which is made from cuminol, an aldehyde found in the oil of caraway.

### ALDEHYDES OF THE BENZENE SERIES.

The aldehydes of this group are closely related to the alcohols just considered. The simplest one is the oil of bitter almonds, or benzoic aldehyde, $C_7H_6O$.

**Oil of bitter almonds, Benzoic aldehyde,** $C_7H_6O (= C_6H_5.CHO)$. — This substance occurs in combination in amygdalin, which is found in bitter almonds, laurel leaves, cherry kernels, etc. Amygdalin belongs to the class of bodies known as *glucosides*, which break up into a glucose and other substances. Amygdalin itself, under the influence of emulsin, which occurs with it in the plants, breaks up into benzoic aldehyde, hydrocyanic acid, and dextrose: —

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2\,H_2O = \underset{\text{Benzoic aldehyde.}}{C_7H_6O} + CNH + \underset{\text{Dextrose.}}{2\,C_6H_{12}O_6}.$$

Benzoic aldehyde may be made:

1. By oxidizing benzyl alcohol: —

$$C_6H_5.CH_2OH + O = C_6H_5.CHO + H_2O.$$

2. By distilling a mixture of calcium benzoate and calcium formate: —

$$\begin{array}{r} C_6H_5.CO\boxed{OM} \\ H.\boxed{COOM} \end{array} = C_6H_5.CHO + M_2CO_3.$$

3. By treating benzoyl chloride, the chloride of benzoic acid, with nascent hydrogen: —

$$C_6H_5.COCl + H_2 = C_6H_5.CHO + HCl.$$

4. By treating benzal chloride with water or mercuric oxide: —

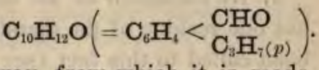
$$C_6H_5.CHCl_2 + H_2O = C_6H_5.CHO + 2\,HCl.$$

NOTE FOR STUDENT. — Refer to the general methods for the preparation of aldehydes. Which of the above reactions are used for the preparation of aldehydes in general? Which of the reactions throw light upon the nature of aldehydes, and their relation to alcohols?

Benzoic aldehyde is prepared either from bitter almonds, which yield about 1.5 to 2 per cent; or from benzal chloride, according to reaction 4, above given. The latter method is employed in the artificial preparation of indigo.

Benzoic aldehyde is a liquid having a pleasant characteristic odor. It boils at 179°; is difficultly soluble in water; is not poisonous.

It unites with oxygen to form benzoic acid; with hydrogen to form benzyl alcohol; with hydrogen sulphide, ammonia, ammonium sulphide, alcohols, acids, anhydrides, and ketones. *In short*, its powers of combination with other substances are almost unlimited. Hence, a very large number of derivatives are known.



**Cuminic aldehyde, cuminol,** $C_{10}H_{12}O\left(=C_6H_4<\begin{matrix}CHO\\C_3H_{7(p)}\end{matrix}\right)$. This aldehyde occurs in oil of caraway, from which it is made. It is a liquid with the odor of the oil of caraway. Its reactions are like those of benzoic aldehyde.

## ACIDS OF THE BENZENE SERIES.

The simplest of these acids has been referred to repeatedly. It is benzoic acid, which bears to benzene the same relation that acetic acid bears to marsh gas. It is the carboxyl derivative of benzene. The homologous acids are the carboxyl derivatives of the homologous hydrocarbons. We shall find mono-basic, bi-basic, tri-basic, and even hexa-basic acids, though the number of acids actually known is small.

## MONOBASIC ACIDS, $C_nH_{2n-8}O_2$.

**Benzoic acid,** $C_7H_6O_2(=C_6H_5.CO_2H)$. — Benzoic acid occurs in gum benzoin, in the balsams of Peru and Tolu, and in combination with amido-acetic acid or glycin in the urine of herbivorous animals. It may be made in many ways, the most important of which are stated below: —

1. By oxidation of benzyl alcohol or any alcohol which is a phenyl derivative of an alcohol of the methyl alcohol series. The common condition in all these alcohols is the presence of the difficultly oxidizable residue, $C_6H_5$, in combination with an easily oxidizable residue of an alcohol of the marsh-gas series: —

$C_6H_5.CH_2OH$ gives $C_6H_5.CO_2H$;
$C_6H_5.CH_2.CH_2OH$ " $C_6H_5.CO_2H$;
$C_6H_5.CH_2.CH_2.CH_2OH$ " $C_6H_5.CO_2H$, etc.

2. By oxidation of benzoic aldehyde, and the aldehydes of the other alcohols referred to in the preceding paragraph.

3. By oxidation of all benzene hydrocarbons which contain but one residue of the marsh-gas series. Attention has already been called to this fact (see p. 246).

4. By treating cyan-benzene (phenyl cyanide, benzo-nitrile) with a caustic alkali (see Exp. 65, p. 267):—

$$C_6H_5CN + KOH + H_2O = C_6H_5.CO_2K + NH_3.$$

5. By treating benzene with carbonyl chloride in the presence of aluminium chloride:—

$$C_6H_6 + COCl_2 = C_6H_5.COCl + HCl;$$
$$C_6H_5.COCl + H_2O = C_6H_5.CO_2H + HCl.$$

A reaction similar to this is of extensive application in the preparation of some hydrocarbons. It will be spoken of more fully under the head of Tri-phenyl-methane.

6. By treating benzene with carbon dioxide in the presence of aluminium chloride:—

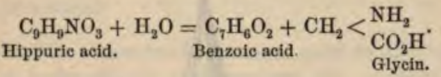
$$C_6H_6 + CO_2 = C_6H_5.CO_2H.$$

This and the preceding methods are of special interest from the scientific stand-point, for the reason that they clearly show the relation which exists between benzoic acid, on the one hand, and benzene and carbonic acid, on the other.

NOTE FOR STUDENT.—Which of the methods above given are of general application for the preparation of the acids of carbon?

Benzoic acid is prepared on the large scale: (1) from gum benzoin by sublimation; (2) from the urine of horses and cows by treating the hippuric acid with hydrochloric acid; (3) from toluene, best, by converting it into benzyl chloride, and oxidizing this with dilute nitric acid.

**Experiment 69.** If the material is obtainable, evaporate a quantity of the urine of horses or cows to about one-half or one-third its volume. Add hydrochloric acid. On cooling, hippuric acid will be deposited. Recrystallize this several times from dilute nitric acid. Boil the hippuric acid for about a quarter of an hour with ordinary concentrated hydrochloric acid. By this means the hippuric acid is decomposed, yielding glycin (amido-acetic acid) and benzoic acid: —



$$\underset{\text{Hippuric acid.}}{C_9H_9NO_3} + H_2O = \underset{\text{Benzoic acid.}}{C_7H_6O_2} + \underset{\text{Glycin.}}{CH_2<\begin{matrix}NH_2\\CO_2H\end{matrix}}.$$

Benzoic acid forms lustrous laminæ or needles, which melt at 121°.

**Experiment 70.** Compare the melting-points of the two specimens of benzoic acid which have been made: (1) from phenyl cyanide (Exp. 65), and (2) from urine. If they are not the same, recrystallize the specimens from water until the melting-points are not changed by further crystallization. Those specimens which are least pure may be purified by recrystallizing them from dilute nitric acid.

The acid is comparatively easily soluble in hot water, but difficultly soluble in cold water. It is volatile with water vapor.

**Experiment 71.** Put some in a one-litre flask, with about $700^{cc}$ to $800^{cc}$ water. Connect with a condenser, and boil down to about $200^{cc}$. Neutralize the distillate with ammonia, and evaporate down to a small volume. Acidify, when benzoic acid will be thrown down.

Its vapor acts upon the mucous membrane of the respiratory passages, producing coughing.

It sublimes very easily.

**Experiment 72.** Put some dry benzoic acid in a small, dry crystallizing dish, and put the dish in a sand-bath. Over the mouth of the dish put a paper cone made from filter-paper, arranged as shown in Fig. 16. Heat with a small flame. The benzoic acid will be deposited on the paper in beautiful lustrous needles.

Or another form of apparatus, which is useful for subliming small quantities of substance, consists, essentially, of two watch-glasses which are of exactly the same size. The edges of the glasses are ground to secure a good joint when they are brought together. In using this apparatus, put the substance to be sublimed in one of the glasses; stretch a round piece of filter-paper over it, and then place the other glass upon it. Clamp the glasses together by means of a thin brass clamp. Now put the glasses on a sand-bath, and warm gently, when the substance will slowly pass through the paper and appear in crystals in the upper watch-glass. It is well to keep a small pad of moist filter-paper on the upper glass during the operation.

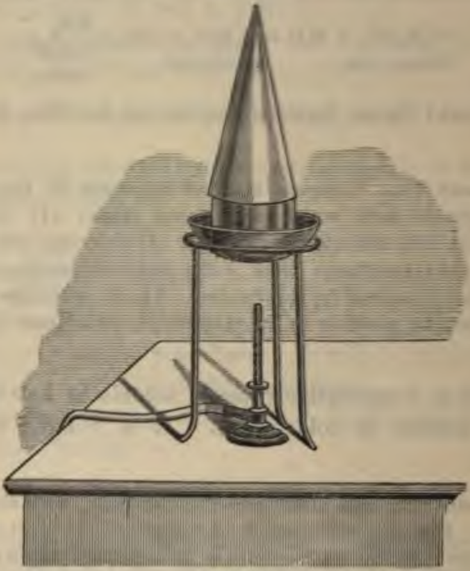


Fig. 16.

When heated with lime, benzoic acid breaks up into benzene and carbon dioxide (see Exp. 55): —

$$C_7H_6O_2 = C_6H_6 + CO_2.$$

With sodium amalgam, it yields benzyl alcohol and other reduction-products. With hydriodic acid, it yields toluene, and then hydrogen addition-products of toluene.

A great many derivatives of benzoic acid are known.

Nearly all its salts are soluble in water.

The ethereal salts may be made by any of the general methods already described.

NOTE FOR STUDENT. — What are the general methods for the preparation of ethereal salts?

**Experiment 73.** Dissolve 40g benzoic acid in 150cc absolute alcohol. Pass *dry* hydrochloric acid gas into the solution, keeping the latter cool by surrounding it with water. When the solution is *saturated* with hydrochloric acid, connect the flask with an inverted condenser, and warm gently on a water-bath for half an hour. Now add three or four volumes of water, when ethyl benzoate will separate as an oil. Wash with water and a little sodium carbonate; and, finally, dry.

**Benzoyl chloride, $C_6H_5.COCl$,** and *bromide*, $C_6H_5.COBr$, are made from benzoic acid in the same way that acetyl chloride is made from acetic acid. They are more stable than the corresponding compounds of the fatty acids, but in general undergo the same kinds of change.

**Benzoyl cyanide, $C_6H_5.CO.CN$,** is made by distilling mercuric cyanide and benzoyl chloride: —

$$2\,C_6H_5.COCl + Hg(CN)_2 = 2\,C_6H_5.COCN + HgCl_2.$$

The cyanogen can be converted into carboxyl, and thus an acid of the formula $C_6H_5.CO.CO_2H$ obtained. This is known as *benzoyl-formic* acid. It is of interest, for the reason that one of its derivatives is also a derivative of indigo (see Isatine).

### *Substitution-Products of Benzoic Acid.*

Benzoic acid readily yields substitution-products when treated with the halogens, nitric acid, and sulphuric acid. The products obtained by direct substitution mostly belong to the meta series. Thus, when chlorine acts upon benzoic acid, the main product is *meta-chlor-benzoic acid;* nitric acid gives mainly *meta-nitro-*

*benzoic acid;* and sulphuric acid gives mainly *meta-sulpho-benzoic acid.*

NOTE FOR STUDENT. — Compare this with the result of the direct action of the same reagents on toluene. What are the first products of the action of nitric and sulphuric acids on toluene?

Substituted benzoic acids may be made, also, by oxidizing the corresponding substituted toluenes. Thus, chlor-toluene gives chlor-benzoic acid; nitro-toluene gives nitro-benzoic-acid, etc.: —

$$C_6H_4Cl.CH_3 \quad \text{gives} \quad C_6H_4Cl.CO_2H;$$
$$C_6H_4(NO_2)CH_3 \quad \text{``} \quad C_6H_4(NO_2)CO_2H.$$

The three *nitro-benzoic acids* and the corresponding *amido-benzoic acids* may serve as examples of the mono-substitution products.

**Ortho-nitro-benzoic acid,** $C_7H_5NO_4\left(= C_6H_4 < \begin{matrix} CO_2H \\ NO_{2(o)} \end{matrix}\right)$. Ortho-nitro-benzoic acid is formed, together with a large quantity of the meta acid and some of the para acid, by treating benzoic acid with nitric acid, by oxidizing ortho-nitro-toluene with potassium permanganate, and by oxidizing ortho-nitro-cinnamic acid. It crystallizes in needles, melts at 147°, and has an intensely sweet taste.

**Meta-nitro-benzoic acid,** $C_6H_4 < \begin{matrix} CO_2H \\ NO_{2(m)} \end{matrix}$, is the chief product of the action of nitric acid on benzoic acid. It crystallizes in laminæ, or plates, and melts at 140° to 141°.

**Para-nitro-benzoic acid,** $C_6H_4 < \begin{matrix} CO_2H \\ NO_{2(p)} \end{matrix}$, is prepared best by oxidizing para-nitro-toluene. It crystallizes in laminæ, melts at 238°, and is much less easily soluble in water than the ortho and meta acids.

*The determination* of the series to which these three acids belong is effected by transforming them into the amido-acids; and these, through the diazo compounds, into the corresponding hydroxy-acids of the formula $C_6H_4 < {OH \atop CO_2H}$.

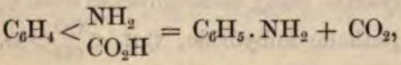
Note for Student. — Give the equations representing the action involved in passing from toluene to ortho-hydroxy-benzoic acid (salicylic acid) by the method above referred to.

In a similar way, lines of connection can be established between the three hydroxy-acids and the chlor-, brom-, and iodo-benzoic acids.

Note for Student. — What are the reactions?

The three hydroxy-acids, on the other hand, have been made by methods which connect them directly with the three bibasic acids of benzene, $C_6H_4 < {CO_2H \atop CO_2H}$, which, in turn, have been made from the three xylenes.

**Ortho-amido-benzoic acid, Anthranilic acid,** $\left.\right\} C_7H_7NO_2 \left(= C_6H_4 < {CO_2H \atop NH_{2(o)}}\right)$. This acid is made by reducing ortho-nitro-benzoic acid with tin and hydrochloric acid, and by boiling indigo with caustic potash. It has already been stated that indigo yields aniline. Now, as ortho-amido-benzoic acid is also obtained, and this breaks up easily into aniline and carbon dioxide,

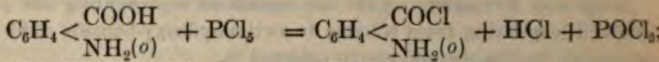


$$C_6H_4 < {NH_2 \atop CO_2H} = C_6H_5 . NH_2 + CO_2,$$

it seems probable that the aniline is a secondary product.

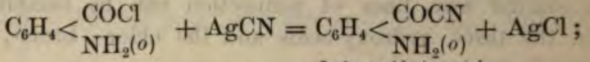
**Isatine,** $C_8H_5NO_2 \left(= C_6H_4 < {CO \atop N} \gg C.OH\right)$. — Isatine is obtained by the oxidation of indigo, and from ortho-amido-benzoic acid as follows: —

The amido-acid is converted into the chloride, the chloride into the cyanide, and this into the corresponding carboxyl derivative, which is the ortho-amido derivative of benzoyl-formic acid. The ortho-amido-benzoyl-formic acid thus obtained loses water, and is converted into isatine. The changes are represented by these equations: —

(1)


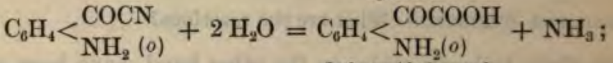
$$C_6H_4<\substack{COOH\\NH_2(o)} + PCl_5 = C_6H_4<\substack{COCl\\NH_2(o)} + HCl + POCl_3;$$

Ortho-amido-benzoic acid. Ortho-amido-benzoyl chloride.

(2)


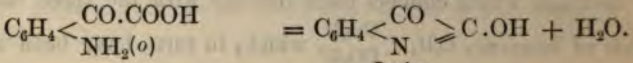
$$C_6H_4<\substack{COCl\\NH_2(o)} + AgCN = C_6H_4<\substack{COCN\\NH_2(o)} + AgCl;$$

Ortho-amido-benzoyl cyanide.

(3)


$$C_6H_4<\substack{COCN\\NH_2\ (o)} + 2\,H_2O = C_6H_4<\substack{COCOOH\\NH_2(o)} + NH_3;$$

Ortho-amido-benzoyl-formic acid.

(4)


$$C_6H_4<\substack{CO.COOH\\NH_2(o)} = C_6H_4<\substack{CO\\N}\geq C.OH + H_2O.$$

Isatine.

The formula given for isatine represents it as an anhydride of ortho-amido-benzoyl-formic acid, the water which is given off being supposed to be formed by a union of the two hydrogens of the amido group and an oxygen of carbonyl. The formation of anhydrides of aromatic acids is a characteristic of ortho compounds. Neither the meta nor para compounds give up water. We shall find that this fact is illustrated in the case of the bibasic acids, the only one which yields an anhydride being ortho-phthalic acid, $C_6H_4<\substack{COOH\\COOH(o)}$, which gives phthalic anhydride, $C_6H_4<\substack{CO\\CO}>O$. This ready formation of anhydrides from ortho compounds, taken together with the fact that the meta and para compounds do not yield anhydrides, has been regarded as an argument in favor of the view that in the ortho compounds the two substituting groups are actually nearer together than in the meta and para compounds.

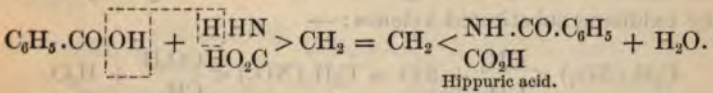
The relation of isatine to indigo will be considered briefly *under* the head of Indigo.

**Meta- and Para-amido-benzoic acids** are made from the corresponding nitro acids by reduction.

**Hippuric acid, benzoyl-amido-acetic acid,**
**$C_9H_9NO_3$(= $C_6H_5$.CONH.$CH_2CO_2H$).**
Hippuric acid, as has already been seen (Exp. 69), occurs in the urine of herbivorous animals, as the cow, horse, camel, and sheep. Some hippuric acid is found in human urine under ordinary circumstances. If benzoic acid be taken with the food, it appears as hippuric acid in the urine, while derivatives of benzoic acid appear as derivatives of hippuric acid.

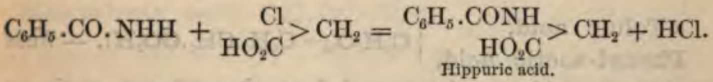
Hippuric acid can be made synthetically from benzoic acid and acetic acid:

1. By heating glycine with benzoic acid to 160° : —



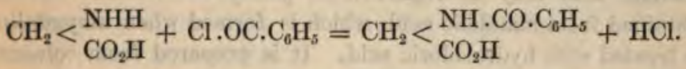
$$C_6H_5.CO\boxed{OH} + \begin{matrix}\boxed{H}HN\\ HO_2C\end{matrix}\!>CH_2 = \underset{\text{Hippuric acid.}}{CH_2<\begin{matrix}NH.CO.C_6H_5\\ CO_2H\end{matrix}} + H_2O.$$

2. By heating benzamide with chlor-acetic acid : —



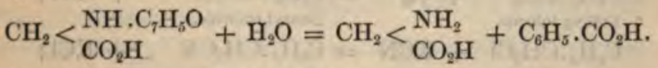
$$C_6H_5.CO.NHH + \begin{matrix}Cl\\ HO_2C\end{matrix}\!>CH_2 = \underset{\text{Hippuric acid.}}{\begin{matrix}C_6H_5.CONH\\ HO_2C\end{matrix}\!>CH_2} + HCl.$$

3. By heating glycine with benzoyl chloride : —



$$CH_2<\begin{matrix}NHH\\ CO_2H\end{matrix} + Cl.OC.C_6H_5 = CH_2<\begin{matrix}NH.CO.C_6H_5\\ CO_2H\end{matrix} + HCl.$$

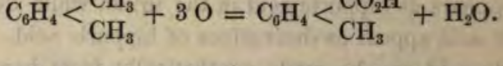
Hippuric acid crystallizes from water in long, rhombic prisms. It is decomposed into benzoic acid and glycine by boiling with alkalies, and more readily by boiling with strong acids (Exp. 69) : —



$$CH_2<\begin{matrix}NH.C_7H_5O\\ CO_2H\end{matrix} + H_2O = CH_2<\begin{matrix}NH_2\\ CO_2H\end{matrix} + C_6H_5.CO_2H.$$

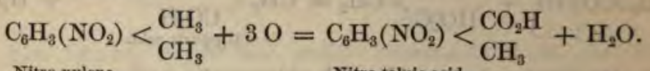
NOTE FOR STUDENT. — What relation does hippuric acid bear to benzamide? What is the effect of boiling acid amides with alkalies? Write the equation for the decomposition of benzamide, and compare it with that for the decomposition of hippuric acid.

**Toluic acids, $C_8H_8O_2$.** — There are four acids of this formula known; viz.; the three carboxyl derivatives of toluene in which the carboxyl takes the place of benzene hydrogen atoms, $C_6H_4 < \genfrac{}{}{0pt}{}{CH_3}{CO_2H}$, and an acid obtained from toluene by replacing a hydrogen of the methyl by carboxyl, thus, $C_6H_5.CH_2.CO_2H$. *Ortho-*, *meta-*, and *para-toluic acids*, $C_6H_4 < \genfrac{}{}{0pt}{}{CH_3}{CO_2H}$, are made by oxidizing the corresponding xylenes with nitric acid: —



$$C_6H_4 < \genfrac{}{}{0pt}{}{CH_3}{CH_3} + 3\,O = C_6H_4 < \genfrac{}{}{0pt}{}{CO_2H}{CH_3} + H_2O.$$

They, as well as their derivatives, of which many are known, have been studied carefully. The substituted toluic acids may be made either by treating the acids with strong reagents or by oxidizing substituted xylenes: —



$$C_6H_3(NO_2) < \genfrac{}{}{0pt}{}{CH_3}{CH_3} + 3\,O = C_6H_3(NO_2) < \genfrac{}{}{0pt}{}{CO_2H}{CH_3} + H_2O.$$

Nitro-xylene. Nitro-toluic acid.

**α-Toluic acid, Phenyl-acetic acid,** } $C_8H_8O_2 (= C_6H_5.CH_2.CO_2H)$. — Just as benzoic acid may be regarded as phenyl-formic acid, so α-toluic acid may be regarded as phenyl-acetic acid. It is obtained from mandelic acid, which is formed when amygdalin is treated with hydrochloric acid. It is prepared from toluene by converting this into benzyl chloride, from which the cyanide is made by boiling with potassium cyanide. The cyanide is then treated with an alkali, and yields the acid: —

$$C_6H_5.CH_3 + Cl_2 = C_6H_5.CH_2Cl + HCl;$$

Boiling toluene. Benzyl chloride.

$$C_6H_5.CH_2Cl + KCN = C_6H_5.CH_2CN + KCl;$$

Benzyl cyanide.

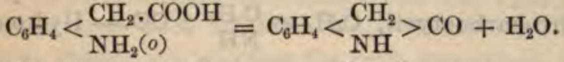
$$C_6H_5.CH_2CN + 2\,H_2O = C_6H_5.CH_2.CO_2H + NH_3.$$

α-Toluic acid.

*The acid* crystallizes in thin laminæ; melts at 76.5°.

Note for Student. — What would you expect α-toluic acid to yield when oxidized? (See p. 246.) What would you expect it to yield when distilled with lime? What would you expect the three toluic acids, $C_6H_4 < {CH_3 \atop CO_2H}$, to yield by oxidation, and when distilled with lime? (See p. 243.)

**Oxindol,** $C_8H_7NO\left(= C_6H_4 < {CH_2 \atop NH} > CO\right)$. — Oxindol is obtained by reduction of isatine (see p. 289); and also from ortho-amido-α-toluic acid by loss of water, in the same way that isatine is formed from ortho-amido-benzoyl-formic acid. When α-toluic acid is treated with nitric acid, the para- and ortho-nitro acids are formed. The latter is reduced by means of tin and hydrochloric acid, when oxindol is at once obtained: —



$$C_6H_4 < {CH_2.COOH \atop NH_2(o)} = C_6H_4 < {CH_2 \atop NH} > CO + H_2O.$$

Ortho-amido-α-toluic acid. Oxindol.

**Mesitylenic acid,** $C_9H_{10}O_2\left(= C_6H_3 \left\{ {(CH_3)_2 \atop CO_2H} \right.\right)$. — This acid has already been referred to as the first product of oxidation of mesitylene. It is the only monobasic acid which has been obtained from mesitylene; and, according to the accepted hypothesis, it is the only one possible. By distillation with lime, it yields meta-xylene.

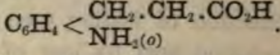
Note for Student. — Of what special significance is the formation of meta-xylene from mesitylenic acid?

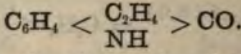
**Hydro-cinnamic acid,**
**Phenyl-propionic acid,** $\Big\}\ C_9H_{10}O_2(= C_6H_5.CH_2.CH_2.CO_2H)$.

Hydro-cinnamic or phenyl-propionic acid is obtained by treating cinnamic acid with nascent hydrogen: —

$$\underset{\text{Cinnamic acid, Phenyl-acrylic acid.}}{C_6H_5.CH.CH.CO_2H} + H_2 = \underset{\text{Hydro-cinnamic acid, Phenyl-propionic acid.}}{C_6H_5.CH_2.CH_2.CO_2H}.$$

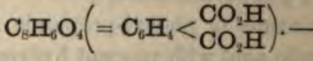
It is also made by starting from ethyl-benzene, $C_6H_5.C_2H_5$, and using the same reactions that are necessary to transform toluene into α-toluic acid (see p. 292). It is a product of the decay of several animal substances, such as albumin, fibrin, brain, etc. It crystallizes from water, in long needles, which melt at 47°. It yields benzoic acid when oxidized.

**Ortho-amido-hydro-cinnamic acid,**  $C_6H_4<\begin{matrix}CH_2.CH_2.CO_2H\\NH_{2(o)}\end{matrix}$.—This acid is prepared from hydro-cinnamic acid in the same way that ortho-amido-α-toluic acid is made from α-toluic acid. It is not obtained in the free state; but, like the ortho-amido derivatives of benzoyl-formic and of α-toluic acids, it loses water, and forms the anhydride,

**Hydro-carbostyril,**  $C_6H_4<\begin{matrix}C_2H_4\\NH\end{matrix}>CO$. — Hydro-carbostyril is made by treating ortho-nitro-hydro-cinnamic acid with tin and hydrochloric acid. It is a solid which crystallizes in prisms, melting at 160°. It is interesting chiefly for the reason that it is closely related to the important compound *quinoline* (which see). When treated with phosphorus pentachloride, hydro-carbostyril is converted into di-chlor-quinoline. The significance of this reaction will be spoken of hereafter.

## BIBASIC ACIDS, $C_nH_{2n-10}O_4$.

The simplest acids of this group are the three phthalic acids, which are the di-carboxyl derivatives of benzene, belonging to the ortho, meta, and para series.

**Phthalic acid,**
**Ortho-phthalic acid,**  $C_8H_6O_4\left(=C_6H_4<\begin{matrix}CO_2H\\CO_2H\end{matrix}\right)$.—Phthalic acid was the first of the three acids of this composition discovered; and, as it was obtained from naphthalene, it was named phthalic acid. In addition to its formation from

naphthalene may be mentioned that from alizarin and purpurin; and from ortho-toluic acid, $C_6H_4 < \substack{CH_3 \\ CO_2H(o)}$, by oxidation with potassium permanganate.

**Experiment 74.** Mix 40g naphthalene and 80g potassium chlorate, and add this mixture *gradually* to 400g ordinary concentrated hydrochloric acid. Naphthalene tetra-chloride, $C_{10}H_8.Cl_4$, is formed in this reaction. Wash with water. *Gradually* add 400g ordinary concentrated nitric acid (sp. gr. 1.45), and boil in a flask connected with an inverted condenser. When all is dissolved, evaporate the nitric acid; and, finally, distil the residue. Phthalic anhydride passes over. Recrystallize from water. This will be used for other experiments.

Phthalic acid forms rhombic crystals, which melt at 213° or lower, according to circumstances, as, when heated, it breaks up gradually, even below the melting-point, into water and the anhydride which melts at 128°. Distilled with lime, it yields benzene; though, by selecting the right proportions, benzoic acid may be obtained: —

$$(1)\qquad C_6H_4 < \substack{CO_2H \\ CO_2H} = C_6H_6 + 2\,CO_2;$$

$$(2)\qquad C_6H_4 < \substack{CO_2H \\ CO_2H} = C_6H_5.CO_2H + CO_2.$$

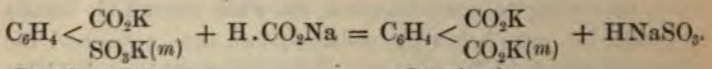
Phthalic acid is decomposed by chromic acid, yielding only carbon dioxide and water. Hence, ortho-xylene, when treated with chromic acid, does not yield phthalic acid. By boiling ortho-xylene with nitric acid, however, it yields ortho-toluic acid, $C_6H_4 < \substack{CH_3 \\ CO_2H(o)}$, and this may be oxidized to phthalic acid by treatment with potassium permanganate.

**Phthalic anhydride,** $C_6H_4 < \substack{CO \\ CO} > O$, is formed by heating phthalic acid. It forms long needles, which melt at 128°. Treated with phenols, it forms the compounds known as *phthaleïns* (which see).

**Isophthalic acid, Meta-phthalic acid,** $\left.\right\} C_6H_4<\begin{matrix}CO_2H\\CO_2H_{(m)}\end{matrix}$, is formed by oxidizing either meta-xylene or meta-toluic acid with chromic acid; by distilling meta-benzene-disulphonic acid with potassium cyanide, and boiling the resulting dicyanide with an alkali.

Note for Student. — Write the equations representing the action involved in passing from meta-benzene-disulphonic acid to isophthalic acid. Into which dihydroxy-benzene is this same disulphonic acid converted by melting it with caustic potash?

The acid is formed, further, by treating meta-sulpho-benzoic acid with sodium formate: —



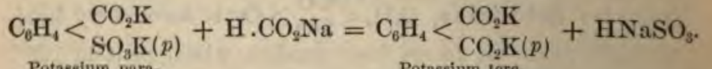
$$C_6H_4<\begin{matrix}CO_2K\\SO_3K(m)\end{matrix} + H.CO_2Na = C_6H_4<\begin{matrix}CO_2K\\CO_2K(m)\end{matrix} + HNaSO_3.$$

Potassium sulpho-benzoate. Potassium isophthalate.

This reaction is of importance, for the reason that the same sulpho-benzoic acid, which is thus converted into isophthalic acid, can be converted also into one of the three hydroxy-benzoic acids; and thus connection is established between the latter and isophthalic acid and meta-xylene.

Isophthalic acid crystallizes in fine needles from water. It melts above 300°, and is not converted into an anhydride.

**Terephthalic acid, Para-phthalic acid,** $\left.\right\} C_6H_4<\begin{matrix}CO_2H\\CO_2H(p)\end{matrix}$. — Terephthalic acid is formed by oxidation of the oil of turpentine,[1] cymene, para-xylene, and para-toluic acid; by heating a mixture of potassium para-sulpho-benzoate and sodium formate: —



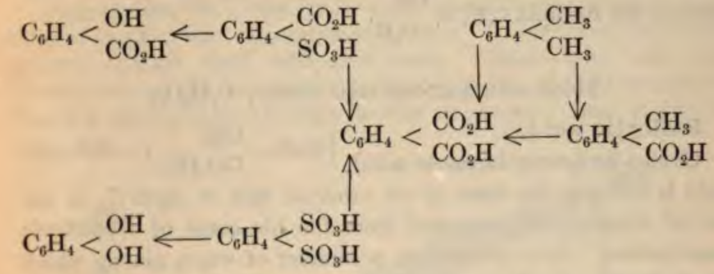
$$C_6H_4<\begin{matrix}CO_2K\\SO_3K(p)\end{matrix} + H.CO_2Na = C_6H_4<\begin{matrix}CO_2K\\CO_2K(p)\end{matrix} + HNaSO_3.$$

Potassium para-sulpho-benzoate. Potassium terephthalate.

---

[1] The prefix *tere* is derived from the Latin *terebinthinus*, turpentine.

Para-sulpho-benzoic acid is converted into one of the three hydroxy-benzoic acids by caustic potash. In the para as well as the meta series, the lines of connection indicated below have been established: —



$$\begin{tikzcd}
C_6H_4 < \begin{matrix} OH \\ CO_2H \end{matrix} & C_6H_4 < \begin{matrix} CO_2H \\ SO_3H \end{matrix} \arrow[l] \arrow[d] & C_6H_4 < \begin{matrix} CH_3 \\ CH_3 \end{matrix} \arrow[dl] \arrow[d] \\
 & C_6H_4 < \begin{matrix} CO_2H \\ CO_2H \end{matrix} & C_6H_4 < \begin{matrix} CH_3 \\ CO_2H \end{matrix} \arrow[l] \\
C_6H_4 < \begin{matrix} OH \\ OH \end{matrix} & C_6H_4 < \begin{matrix} SO_3H \\ SO_3H \end{matrix} \arrow[l] \arrow[u] &
\end{tikzcd}$$

Terephthalic acid is a solid which is practically insoluble in water. It sublimes without melting and, like isophthalic acid, yields no anhydride.

### HEXABASIC ACID.

**Mellitic acid, $C_{12}H_6O_{12}[= C_6(CO_2H)_6]$.** — This acid occurs in nature in the form of the aluminium salt, as the mineral *honey-stone* or *mellite*. The mineral is rare, and is found in beds of lignite. Mellitic acid has been made by direct oxidation of carbon with potassium permanganate, and by oxidation of hexa-methyl-benzene, $C_6(CH_3)_6$. By ignition with soda-lime it is converted into benzene and carbon dioxide: —

$$C_6(CO_2H)_6 = C_6H_6 + 6\,CO_2.$$

### PHENOL-ACIDS, OR HYDROXY-ACIDS OF THE BENZENE SERIES.

It will be remembered that the alcohol acids or hydroxy-acids of the paraffin series form an important class, including such compounds as glycolic, lactic, malic, tartaric, and citric acids. The peculiarity of these compounds is their double character. They are at the same time alcohols and acids, though the acid properties are more prominent than the alcoholic. The hydroxy-acids of the benzene series bear the same relations to the benzene hydrocarbons that the hydroxy-acids already considered bear to the paraffins. The simplest are those which contain one hydroxyl and one carboxyl in benzene, having the formula $C_6H_4<\begin{matrix}OH\\CO_2H\end{matrix}$.

### MONO-HYDROXY-BENZOIC ACIDS, $C_7H_6O_3$.

**Salicylic acid, Ortho-hydroxy-benzoic acid,** $\left.\right\} C_6H_4<\begin{matrix}OH\\CO_2H_{(o)}\end{matrix}$. — Salicylic acid is found in the form of an ethereal salt of methyl, in the oil of wintergreen, prepared from the blossoms of *Gaultheria procumbens*. It is formed in a number of ways, among which the following should be specially mentioned: —

1. By converting ortho-amido-benzoic acid into the diazo compound, and boiling with water.

NOTE FOR STUDENT. — Give the equations representing the reactions.

2. By melting ortho-sulpho-benzoic acid with caustic potash.

NOTE FOR STUDENT. — Write the equation.

3. By passing carbon dioxide over sodium phenolate heated to 180°: —

$$2\,C_6H_5.ONa + CO_2 = C_6H_4<\begin{matrix}ONa\\CO_2Na\end{matrix} + C_6H_5OH.$$

4. By heating phenol with tetra-chlor-methane and alcoholic potash: —

$$C_6H_5.OH + CCl_4 + 6\,KOH = C_6H_4<\begin{matrix}OK\\CO_2K\end{matrix} + 4\,KCl + 4\,H_2O.$$

5. By saponifying the methyl salicylate found in the oil of wintergreen: —

$$C_6H_4<\begin{matrix}OH\\CO_2CH_3\end{matrix} + KOH = C_6H_4<\begin{matrix}OH\\CO_2K\end{matrix} + CH_3OH.$$

**Experiment 75.** Boil 30^cc^ to 40^cc^ oil of wintergreen with moderately strong caustic potash in a flask connected with an inverted condenser. When it is dissolved, acidify with hydrochloric acid. Filter off the salicylic acid which separates, and recrystallize from water.

**Experiment 76.** Dissolve 50$^g$ to 60$^g$ phenol in the equivalent quantity of caustic soda. Evaporate to dryness. Powder, and put the salt in two or three small, flat-bottom flasks. Connect these with each other, and pass dry carbon dioxide through them. For the purpose of heating them, it is best to place them in an air-bath. Heat at first to 100°, and then gradually let the temperature rise to 180°. Finally, heat to 220° to 250°. After cooling, dissolve the mass in not too much water, and add hydrochloric acid. Salicylic acid will separate. Recrystallize from water, with the addition of bone-black.

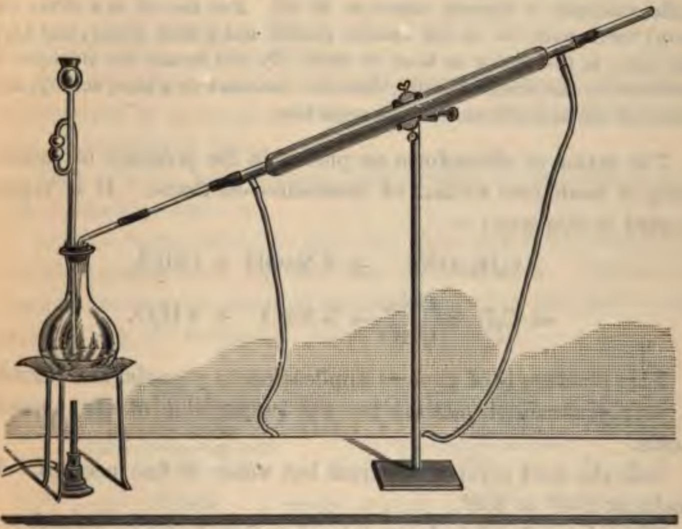
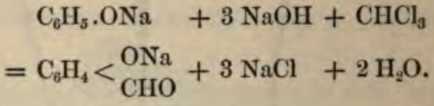


Fig. 17.

**Experiment 77.** Make a solution of 40$^g$ phenol and 80$^g$ sodium hydroxide in 120$^{cc}$ to 140$^{cc}$ water. Add gradually 60$^g$ chloroform, constantly shaking the mixture. The solution changes color, and becomes, finally, deep red. The flask should be arranged as shown in Fig. 17, to prevent loss of chloroform in consequence of the spontaneous elevation of temperature. After all the chloroform is used up, and the action is over, boil for half an hour. Add dilute hydrochloric or sulphuric acid until the solution has an acid reaction. A thick, red-colored oil will be thrown down. Boil by passing steam through the liquid, as in Exp. 67. A light-colored oil will pass over. This is the *aldehyde* of salicylic acid, together with some unacted-upon phenol. Dissolve in ether, and shake this with an aqueous solution of mono-sodium sulphite, when the aldehyde unites with the sulphite. Separate the ether solution of phenol from the lower water solution, and acidify the latter with hydrochloric or sulphuric acid, when salicylic aldehyde is thrown down as an oil. Put the oil in a silver (or iron) basin with $20^g$ to $30^g$ caustic potash and a little water, and keep the mass in fusion for an hour or two. By this means the aldehyde is oxidized to the acid. Finally, dissolve the mass in water, acidify, and filter off the salicylic acid which separates.

The action of chloroform on phenol in the presence of caustic soda is analogous to that of tetra-chlor-methane. It is represented in this way: —

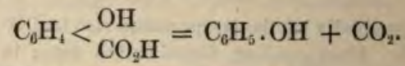


$$\begin{aligned} &C_6H_5.ONa \quad + 3\,NaOH + CHCl_3 \\ &= C_6H_4{<}\begin{matrix}ONa\\CHO\end{matrix} + 3\,NaCl \quad + 2\,H_2O. \end{aligned}$$

This reaction is of general application to phenols, and affords a very convenient method for the preparation of the phenol-acids.

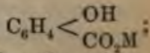
Salicylic acid crystallizes from hot water in fine needles. It melts at 155° to 156°.

When heated, it breaks up into phenol and carbon dioxide: —



$$C_6H_4{<}\begin{matrix}OH\\CO_2H\end{matrix} = C_6H_5.OH + CO_2.$$

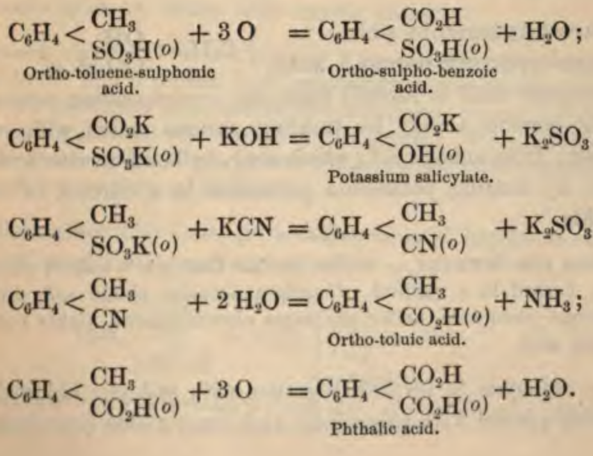
With ferric chloride, its aqueous solution gives a characteristic dark violet-blue color. Free salicylic acid is antiseptic, preventing decay and fermentation. It is therefore used for preserving organic substances.

Salicylic acid forms salts of the general formula  $C_6H_4{<}\begin{matrix}OH\\CO_2M\end{matrix}$; *and, with* the alkalies, compounds, in which both the phenol hydrogen and the acid hydrogen are replaced by metals, as $C_6H_4 < \begin{matrix} OK \\ CO_2K \end{matrix}$. Salts of the latter order, which contain the metals of the alkaline earths, are decomposed by carbon dioxide. Salicylic acid forms ethereal salts of the general formula $C_6H_4 < \begin{matrix} OH \\ CO_2R \end{matrix}$, of which methyl salicylate, $C_6H_4 < \begin{matrix} OH \\ CO_2CH_3 \end{matrix}$, is the best-known example. It forms, also, ether-acids of the general formula $C_6H_4 < \begin{matrix} OR \\ CO_2H \end{matrix}$; and, finally, compounds of the general formula $C_6H_4 < \begin{matrix} OR \\ CO_2R \end{matrix}$.

A very large number of substitution-products and other derivatives of salicylic acid have been studied; but they need not be considered here.

That salicylic acid belongs to the ortho series, follows from the following facts: —

Ortho-toluene-sulphonic acid has been converted into ortho-sulpho-benzoic acid, and this into salicylic acid. Further, the same toluene-sulphonic acid has been converted into ortho-toluic acid, which, by oxidation, yields phthalic acid.



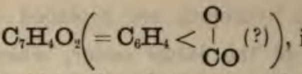
$$(1)\quad \underset{\text{Ortho-toluene-sulphonic acid.}}{C_6H_4 < \begin{matrix} CH_3 \\ SO_3H(o) \end{matrix}} + 3\,O = \underset{\text{Ortho-sulpho-benzoic acid.}}{C_6H_4 < \begin{matrix} CO_2H \\ SO_3H(o) \end{matrix}} + H_2O;$$

$$(2)\quad C_6H_4 < \begin{matrix} CO_2K \\ SO_3K(o) \end{matrix} + KOH = \underset{\text{Potassium salicylate.}}{C_6H_4 < \begin{matrix} CO_2K \\ OH(o) \end{matrix}} + K_2SO_3;$$

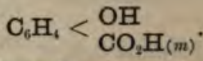
$$(3)\quad C_6H_4 < \begin{matrix} CH_3 \\ SO_3K(o) \end{matrix} + KCN = C_6H_4 < \begin{matrix} CH_3 \\ CN(o) \end{matrix} + K_2SO_3;$$

$$(4)\quad C_6H_4 < \begin{matrix} CH_3 \\ CN \end{matrix} + 2\,H_2O = \underset{\text{Ortho-toluic acid.}}{C_6H_4 < \begin{matrix} CH_3 \\ CO_2H(o) \end{matrix}} + NH_3;$$

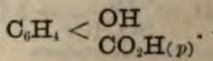
$$(5)\quad C_6H_4 < \begin{matrix} CH_3 \\ CO_2H(o) \end{matrix} + 3\,O = \underset{\text{Phthalic acid.}}{C_6H_4 < \begin{matrix} CO_2H \\ CO_2H(o) \end{matrix}} + H_2O.$$

**Salicylid**, $C_7H_4O_2$  $\left(=C_6H_4<\begin{array}{c}O\\|\\CO\end{array}(?)\right)$, is a substance obtained from salicylic acid by the abstraction of water. This ability to form anhydrides is in some way connected with the ortho relation, as the two isomeric hydroxy-acids do not yield anhydrides.

Note for Student. — Compare the three phthalic acids in this respect.

**Oxybenzoic acid,**
**Meta-hydroxy-benzoic acid,**  $\Big\} C_6H_4<\begin{array}{l}OH\\CO_2H_{(m)}\end{array}$. — This acid is made from meta-amido-benzoic and meta-sulpho-benzoic acid by the usual reactions.

It crystallizes from water in needles united to form wart-like looking masses. It gives no color with ferric chloride. Its connection with meta-phthalic (isophthalic) acid and meta-xylene is effected by means of the transformations tabulated on p. 297; that is to say, the same sulpho-benzoic acid which, by melting with caustic potash, yields oxybenzoic acid, by melting with sodium formate, yields isophthalic acid. Therefore oxybenzoic acid is a meta compound.

**Para-oxybenzoic acid,**
**Para-hydroxy-benzoic acid,**  $\Big\} C_6H_4<\begin{array}{l}OH\\CO_2H_{(p)}\end{array}$. — Para-oxybenzoic acid is formed from the corresponding amido and sulpho-benzoic acids; by treating various resins with caustic potash; from anisic acid (which see), by heating with hydriodic acid; by heating potassium phenolate in a current of carbon dioxide.

Note for Student. — Notice the fact that, while *sodium* phenolate, when heated in a current of carbon dioxide, yields salicylic acid, *potassium* phenolate, under the same circumstances, yields para-oxybenzoic acid.

Its aldehyde is formed, together with salicylic aldehyde, by treating phenol with chloroform and caustic soda (see Exp. 77).

The reasons for considering para-oxybenzoic acid as a member of the para series are similar to those which show that oxybenzoic acid is a meta compound. The same sulpho-benzoic acid which yields para-oxybenzoic acid, also yields terephthalic acid.

**Anisic acid, Para-methoxy-benzoic[1] acid,** $\left.\begin{matrix}\\\\\end{matrix}\right\} C_6H_4 < \begin{matrix} OCH_3 \\ CO_2H_{(p)} \end{matrix}$. — Anisic acid is formed by the oxidation of anethol, $C_6H_4 < \begin{matrix} OCH_3 \\ C_3H_5 \end{matrix}$, a phenol ether contained in anise oil. It is made by heating para-oxybenzoic acid with caustic potash and methyl iodide. As the formula indicates, it is the methyl ether of para-oxybenzoic acid.

### DI-HYDROXY-BENZOIC ACIDS, $C_7H_6O_4$.

**Protocatechuic acid,** $C_6H_3 \left\{ \begin{matrix} (OH)_2 \\ CO_2H \end{matrix} \right.$, is a frequent product of the fusion of organic substances with caustic potash. Thus, the following substances, among others, yield it: oil of cloves, piperic acid, catechin, gum benzoin, asafœtida, vanillin, etc. It is made from sulpho-oxybenzoic acid, and from sulpho-para-oxybenzoic acids by fusing with caustic potash.

NOTE FOR STUDENT. — What analogy is there between the fact that protocatechuic acid is formed from sulpho-oxybenzoic acid and from sulpho-para-oxybenzoic acid, and the fact that pseudocumene is formed from brom-meta-xylene and from brom-para-xylene? What conclusion may be drawn regarding the relations of the two hydroxyl groups, and the carboxyl in protocatechuic acid?

By distillation with lime, protocatechuic acid breaks up into pyrocatechin and carbon dioxide: —

$$C_6H_3 \left\{ \begin{matrix} OH \\ OH \\ CO_2H \end{matrix} \right. = \underset{\text{Pyrocatechin.}}{C_6H_4 \left\{ \begin{matrix} OH \\ OH \end{matrix} \right.} + CO_2.$$

---

[1] *Methoxy* is derived from *methoxyl*, the name given to the ether group, $OCH_3$. In a similar way $OC_2H_5$ is called *ethoxyl*; $OC_6H_5$, *phenoxyl*, etc.

**Vanillic acid,** $C_6H_3\left\{\begin{matrix}OCH_3\\OH\\CO_2H\end{matrix}\right.$, is formed by oxidation of vanillin, which is the corresponding aldehyde. It is the monomethyl ether of protocatechuic acid.

**Vanillin,** $C_8H_8O_3\left(=C_6H_3\left\{\begin{matrix}OCH_3\\OH\\CHO\end{matrix}\right.\right)$, occurs in nature, as a crystalline coating, on the fruit of the vanilla. It is made artificially by treating the ether, $C_6H_4<\begin{matrix}OCH_3\\OH(o)\end{matrix}$, with chloroform and caustic soda.

### TRI-HYDROXY-BENZOIC ACIDS, $C_7H_6O_5$.

**Gallic acid,** $C_7H_6O_5\left(=C_6H_2\left\{\begin{matrix}(OH)_3\\CO_2H\end{matrix}\right.\right)$. — Gallic acid occurs in sumach, and in Chinese tea, and many other plants. It is formed by boiling tannin or tannic acid with sulphuric acid; by melting brom-protocatechuic acid with caustic potash: —

$$\underset{\text{Brom-protocatechuic acid.}}{C_6H_2\left\{\begin{matrix}Br\\(OH)_2\\CO_2H\end{matrix}\right.} + KOH = \underset{\text{Gallic acid.}}{C_6H_2\left\{\begin{matrix}(OH)_3\\CO_2H\end{matrix}\right.} + KBr.$$

It is best prepared from gall nuts by fermentation of the tannin contained in them.

Gallic acid is easily soluble in water. Its solution gives, with a little ferric chloride, a blue-black precipitate, which dissolves in excess of ferric chloride, forming a dark green solution. It readily reduces metallic salts in solution. When heated, it yields pyrogallol (pyrogallic acid) and carbon dioxide: —

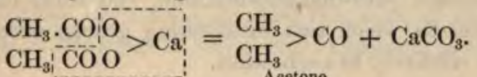
$$C_6H_2\left\{\begin{matrix}(OH)_3\\CO_2H\end{matrix}\right. = C_6H_3(OH)_3 + CO_2.$$

**Tannic acid, tannin,** $C_{14}H_{10}O_9$. — This substance occurs in gall nuts, from which it is extracted in large quantities. It is an amorphous powder. It is markedly astringent in its action on the mucous membranes. It is soluble in water, the solution giving, with ferric chloride, a dark blue-black color. Tannin is used extensively in medicine, in dyeing, and in the manufacture of ink. Its relation to gallic acid is indicated by the following equation: —

$$\underset{\text{Gallic acid.}}{2\,C_7H_6O_5} = \underset{\text{Tannin.}}{C_{14}H_{10}O_9} + H_2O.$$

## KETONES AND ALLIED DERIVATIVES OF THE BENZENE SERIES.

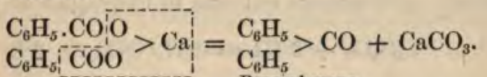
The ketones of the benzene series are strictly analogous to those of the paraffin series, and they are made in the same way. Acetone is made by distilling calcium acetate: —



$$\begin{array}{l}CH_3.CO\,O\\CH_3\,CO\,O\end{array}>Ca = \begin{array}{l}CH_3\\CH_3\end{array}>CO + CaCO_3.$$

Acetone.

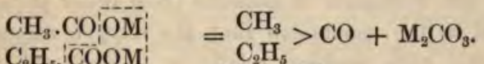
So, also, benzophenone or diphenyl ketone is made by distilling calcium benzoate: —



$$\begin{array}{l}C_6H_5.CO\,O\\C_6H_5\,COO\end{array}>Ca = \begin{array}{l}C_6H_5\\C_6H_5\end{array}>CO + CaCO_3.$$

Benzophenone.

Further, by distilling mixtures of the salts of two fatty acids, mixed ketones are obtained: —

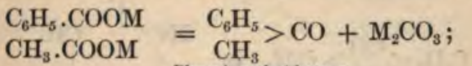


$$\begin{array}{l}CH_3.CO\,OM\\C_2H_5.\,COOM\end{array} = \begin{array}{l}CH_3\\C_2H_5\end{array}>CO + M_2CO_3.$$

Ethyl-methyl ketone.

And, similarly, mixed ketones containing one residue of a benzene hydrocarbon and one of a paraffin; or, two different residues of benzene hydrocarbons may be obtained thus: —

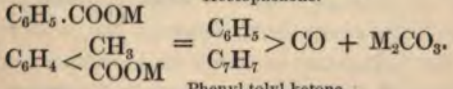
(1)



$$\begin{array}{l}C_6H_5.COOM\\CH_3.COOM\end{array} = \begin{array}{l}C_6H_5\\CH_3\end{array}>CO + M_2CO_3;$$

Phenyl-methyl ketone, Acetophenone.

(2)



$$\begin{array}{l}C_6H_5.COOM\\C_6H_4<\begin{array}{l}CH_3\\COOM\end{array}\end{array} = \begin{array}{l}C_6H_5\\C_7H_7\end{array}>CO + M_2CO_3.$$

Phenyl-tolyl-ketone.

The individual ketones need not be considered.

## Quinones.

The quinones are peculiar bodies which in some ways are allied to the ketones. The simplest example of the class, and the one best known, is called *quinone*. Its formula is $C_6H_4O_2$, and it therefore appears to be benzene in which two hydrogen atoms are replaced by two oxygen atoms. All quinones bear this relation to the hydrocarbons, of which they may be regarded as derivatives.

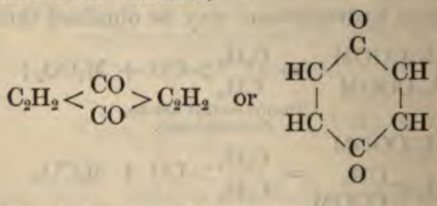
**Quinone, $C_6H_4O_2$,** is formed by the oxidation of quinic acid, hydroquinone, para-diamido-benzene, and some other benzene derivatives in which two substituting groups occupy the *para* position relatively to each other.

It forms long, yellow prisms; sublimes in golden-yellow needles.

Hydriodic acid reduces quinone to hydroquinone: —

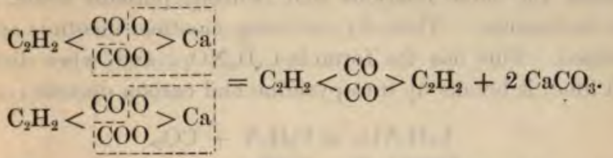
$$C_6H_4O_2 + 2\,HI = C_6H_4(OH)_2 + 2\,I.$$

The easy transformation of hydroquinone into quinone, and the opposite transformation of quinone into hydroquinone, as well as the formation of quinone from other para compounds, force us to the conclusion that the oxygen atoms in quinone are in the para position relatively to each other. Quinone appears, therefore, as a substance containing two *carbonyl* groups which are united by means of hydrocarbon residues, as indicated in the formula, —



$$C_2H_2<\begin{matrix}CO\\CO\end{matrix}>C_2H_2 \quad \text{or}$$

A substance of this kind may be called a *di-ketone*, and may be regarded as derived from a dibasic acid in the same way that a simple ketone is derived from a monobasic acid. Thus, the calcium salt of an acid of the formula $C_2H_2<\genfrac{}{}{0pt}{}{COOH}{COOH}$ ought, according to this view, to yield quinone by distillation: —



$$\begin{array}{l} C_2H_2<\genfrac{}{}{0pt}{}{CO\,O}{COO}>Ca \\ C_2H_2<\genfrac{}{}{0pt}{}{CO\,O}{COO}>Ca \end{array} = C_2H_2<\genfrac{}{}{0pt}{}{CO}{CO}>C_2H_2 + 2\,CaCO_3.$$

Several quinones have been studied. Under the head of Anthracene, we shall meet with an important one called *anthraquinone*, which has been made by such reactions as prove it to be a di-ketone in the sense in which this expression is explained above.

## PYRIDINE BASES, $C_nH_{2n-5}N$.

In the manufacture of bone-black, bones are subjected to dry distillation, when an oil passes over which is known as *bone oil.* This oil is a complex mixture of substances, several of which have, however, been isolated. Among the pure substances which have been obtained from bone oil may be mentioned pyridine, picoline, lutidine, and collidine. All these compounds contain nitrogen; and, starting with pyridine, they form a homologous series: —

| | |
|---|---|
| Pyridine | $C_5H_5N$. |
| Picoline | $C_6H_7N$. |
| Lutidine | $C_7H_9N$. |
| Collidine | $C_8H_{11}N$. |

**Pyridine, $C_5H_5N$.** — Besides being formed in the distillation of bones, pyridine has recently been made in several ways, some of which enable us to form a conception in regard to its relations to other substances which have been considered. Great interest in the substance and its derivatives has been aroused by the observation that several of the alkaloids which occur in nature, such as quinine, cinchonine, nicotine, etc., when oxidized, yield acids containing nitrogen, which bear to pyridine the same relations that benzoic, phthalic acids, etc., bear to benzene. Thus, by oxidizing nicotine, nicotinic acid is obtained. This has the formula $C_6H_5NO_2$; and, when distilled with lime, it breaks up into pyridine and carbon dioxide: —

$$\underset{\text{Nicotinic acid.}}{C_6H_5NO_2} = \underset{\text{Pyridine.}}{C_5H_5N} + CO_2.$$

This naturally leads to the conclusion that nicotinic acid is pyridine-carbonic acid, $C_5H_4N.CO_2H$, which bears to pyridine the same relation that benzoic acid bears to benzene, acetic acid to marsh gas, etc.

Pyridine is formed: —

1. By treating iso-amyl nitrate with phosphorus pentoxide: —

$$C_5H_{11}.NO_3 = C_5H_5N + 3\,H_2O.$$

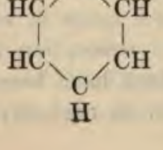
2. By conducting acetylene and hydrocyanic acid together through a tube heated to redness: —

$$2\,C_2H_2 + HCN = C_5H_5N.$$

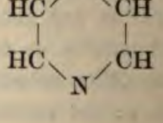
It is a liquid with a peculiar, sharp, characteristic odor. It boils at 116.7°.

It unites with acids forming salts.

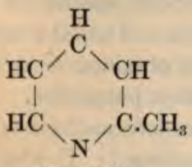
It has been suggested that pyridine is related to benzene; and that it may be regarded as the hydrocarbon in which one of the six CH groups is replaced by a nitrogen atom, as represented in the formulas



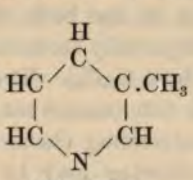
and



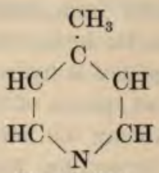
This view has suggested various lines of investigation. Thus, if the above formula really represents the relations between benzene and pyridine, it is clear that the existence of three isomeric mono-substitution products of pyridine ought to be possible. Thus, there should be three methyl-pyridines or picolines, three pyridine-carbonic acids, etc. The three picolines should correspond to the formulas



Ortho-picoline.



Meta-picoline.



Para-picoline.

All three picolines are known; and, by oxidation, they are converted into the three pyridine-carbonic acids, $C_5H_4N.CO_2H$; and these, when distilled with lime, yield pyridine and carbon dioxide.

The pyridine bases unite with two, four, or six atoms of hydrogen. The addition-products thus formed are believed to exist in the alkaloids.

*Piperidine*, $C_5H_{11}N$, a base found in piperine, a constituent of pepper, has been shown to be hexa-hydro-pyridine.

*Nicotine* is probably of similar structure.

Valuable results may be expected from the further investigation of pyridine and its derivatives.

## Terpenes, $C_{10}H_{16}$.

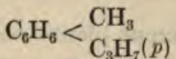
In nature, particularly in the coniferous plants, occur several isomeric hydrocarbons, which are known by the common name *terpene*. These substances are very susceptible to the action of reagents, and hence undergo many changes. One of the most common changes is polymerisation. Thus, when a terpene is heated in a sealed tube, or is shaken with concentrated sulphuric acid, or with boron fluoride and other substances, it is converted into polymeric modifications of the formulas $C_{15}H_{24}$ and $C_{20}H_{32}$. The terpenes unite with hydrochloric and hydrobromic acids, forming compounds, $C_{10}H_{16}.HCl$ and $C_{10}H_{16}.2\,HCl$.

**Oil of turpentine, terebenthene, $C_{10}H_{16}$.** — This oil is obtained by distilling turpentine, a resinous substance which exudes from incisions in the bark of various species of the pine, larch, fir, etc., especially from the pine. The oil consists largely of a hydrocarbon, $C_{10}H_{16}$. The oils obtained from different species of trees differ somewhat in their properties.

Among the more interesting chemical transformations of oil of turpentine, the following may be mentioned: It absorbs oxygen from the air; dilute nitric acid oxidizes it readily, converting it into acetic, propionic, butyric, oxalic, para-toluic, terephthalic acids and some other acids; bromine and iodine convert it into cymene.

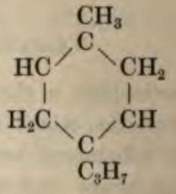
Oil of turpentine is used in the manufacture of varnishes on account of its solvent power for resins. It is also used in medicine.

The reactions above enumerated indicate clearly that there is a close relation between cymene and oil of turpentine. This is shown by the fact that it is so readily converted into cymene, and that it yields para-toluic and terephthalic acids by oxidation. It has therefore been suggested that oil of turpentine is a hydrogen addition-product of cymene, of the formula



$$C_6H_6 < \begin{matrix} CH_3 \\ C_3H_7(p) \end{matrix}$$

or



We know nothing in regard to the causes of the isomerism of the different terpenes.

It should be observed that the above formula furnishes no explanation of the fact that oil of turpentine acts like an unsaturated compound.

**Terpene hydrochloride, Artificial camphor,** $\left.\right\}$ $C_{10}H_{16}.HCl$.—When hydrochloric acid gas is conducted into oil of turpentine, a curious solid known as *artificial camphor* is formed. It looks like ordinary camphor, and has a very similar odor. When heated alone, or with bases, it gives off hydrochloric acid, and a terpene different from the oil of turpentine is formed.

## CAMPHOR.

**Borneol, Borneo camphor, $C_{10}H_{18}O$.** — Borneo camphor is a substance found in cavities in a tree (*Dryobalanops camphora*) which grows in Borneo, Sumatra, etc. It may be made by treating ordinary camphor with sodium: —

$$\underset{\text{Ordinary camphor.}}{2\,C_{10}H_{16}O} + 2\,Na = \underset{\text{Sodium compound of borneol.}}{C_{10}H_{17}ONa} + \underset{\text{Sodium compound of ordinary camphor.}}{C_{10}H_{15}ONa}.$$

The relation between the two kinds of camphor is shown better by the equation: —

$$\underset{\text{Ordinary camphor.}}{C_{10}H_{16}O} + H_2 = \underset{\text{Borneol.}}{C_{10}H_{18}O}.$$

**Camphor, laurinol, $C_{10}H_{16}O$.** — This is the substance ordinarily called *camphor*. It is obtained in China and Japan from different species of the genus *camphora* of the *laurus* family, by distilling the finely-cut wood with water vapor. It is purified by sublimation.

Camphor forms hexagonal crystals; melts at 175°, and boils at 204°. It is only slightly soluble in water; easily soluble in alcohol.

Boiled with iodine, hydriodic acid gas is given off and cymene is formed. Phosphorus pentoxide decomposes camphor into cymene and water: —

$$\underset{\text{Camphor.}}{C_{10}H_{16}O} = \underset{\text{Cymene.}}{C_{10}H_{14}} + H_2O.$$

The same decomposition is effected by heating camphor with concentrated hydrochloric acid to 170°. It will be seen that, as far as the composition is concerned, the difference between a terpene and camphor is one atom of oxygen: —

$$\underset{\text{Terpene.}}{C_{10}H_{16}}. \qquad \underset{\text{Camphor.}}{C_{10}H_{16}O}.$$

The relation between the substances is undoubtedly a close one, as is shown by the formation of cymene from both. It is stated that a substance closely resembling camphor has been made by oxidizing the terpene known as *camphene*, which is formed by shaking oil of turpentine with sulphuric acid.

# CHAPTER XVI.

## DI-PHENYL-METHANE, TRI-PHENYL-METHANE, TETRA-PHENYL-METHANE, AND THEIR DERIVATIVES.

As we have seen, toluene may be regarded either as methyl-benzene or phenyl-methane. Of course, according to all that is known regarding similar substances, the two views are identical. Regarding it, for our present purpose, as phenyl-methane, we may write its formula thus: $C\left\{\begin{array}{l}C_6H_5\\H\\H\\H\end{array}\right.$

This suggests the possibility of the existence of such substances as

*Di-phenyl-methane* . . . . . . . . $C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\H\\H\end{array}\right.$,

*Tri-phenyl-methane* . . . . . . . . $C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_5\\H\end{array}\right.$,

and *Tetra-phenyl-methane* . . . . . . . $C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_5\\C_6H_5\end{array}\right.$.

All these hydrocarbons are known, and the derivatives of tri-phenyl-methane are of special interest and importance.

There is one reaction by means of which these hydrocarbons can be made very readily. It has also been used for the synthesis of many other hydrocarbons. It depends upon the remarkable fact that, when a hydrocarbon is brought together with a compound containing chlorine, and aluminium chloride then added, hydrochloric acid is evolved, and union of the two substances is effected, the aluminium chloride not entering into the composition of the product. Thus, when benzene and benzyl chloride, $C_6H_5.CH_2Cl$, are brought together under ordinary circumstances, no action takes place; but, if some solid aluminium chloride be added, reaction takes place in the sense of the following equation: —

$$C_6H_5.CH_2Cl + C_6H_6 = \underset{\text{Di-phenyl-methane.}}{C_6H_5.CH_2.C_6H_5} + HCl,$$

and di-phenyl-methane is formed.

Similarly, when chloroform and benzene are brought together in the presence of aluminium chloride, tri-phenyl-methane is formed according to this equation: —

$$CHCl_3 + 3\,C_6H_6 = \underset{\text{Tri-phenyl-methane.}}{CH(C_6H_5)_3} + 3\,HCl.$$

Another method by which these hydrocarbons can be made, consists in heating a chloride and a hydrocarbon together in the presence of zinc dust. Thus, benzyl chloride and benzene give di-phenyl-methane when boiled with zinc dust; and benzal chloride, $C_6H_5.CHCl_2$, and benzene give tri-phenyl-methane: —

$$C_6H_5.CHCl_2 + 2\,C_6H_6 = CH(C_6H_5)_3 + 2\,HCl.$$

Only tri-phenyl-methane will be considered.

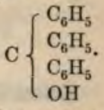
**Tri-phenyl-methane,** $C_{19}H_{16}[= CH(C_6H_5)_3]$. — This hydrocarbon may be made, as above described, from benzal chloride and benzene, and from chloroform and benzene. It may be made also from benzal chloride and mercury diphenyl, $Hg(C_6H_5)_2$: —

$$C_6H_5.CHCl_2 + Hg(C_6H_5)_2 = CH(C_6H_5)_3 + HgCl_2.$$

It forms lustrous, thin laminæ, which melt at 92°. It is insoluble in water; easily soluble in ether and chloroform. It is crystallized best from alcohol.

Towards reagents it is very stable. Thus, ordinary concentrated sulphuric acid does not act upon it.

Oxidizing agents convert it into tri-phenyl-carbinol,



$$C\left\{\begin{array}{l}C_6H_5\\C_6H_5.\\C_6H_5\\OH\end{array}\right.$$

That the oxidation-product is really tri-phenyl-carbinol appears probable, from the fact that whenever aromatic hydrocarbons which contain paraffin residues are oxidized, the paraffin residues are first attacked, while, as a rule, the benzene residue is unacted upon.

**Trinitro-triphenyl-methane,** $C_{19}H_{13}(NO_2)_3[=CH(C_6H_4NO_2)_3]$, is formed by treating tri-phenyl-methane with nitric acid; and also by treating a mixture of nitro-benzene and chloroform with aluminium chloride: —

$$CHCl_3 + 3\,C_6H_5.NO_2 = CH(C_6H_4.NO_2)_3 + 3\,HCl.$$

This reaction shows that in the tri-nitro product one nitro group is contained in each benzene residue.

**Triamido-triphenyl-methane, para-leucaniline,** $C_{19}H_{13}(NH_2)_3[=CH(C_6H_4.NH_2)_3]$.

The tri-amido compound is made by reduction of the tri-nitro compound, and also by reduction of para-rosaniline. It is converted into para-rosaniline by oxidation.

## ANILINE DYES.

The well-known substances included under the head of Aniline Dyes are more or less simple derivatives of the two compounds called *rosaniline* and *para-rosaniline*.

When mixtures of aniline and toluidine are heated together with different oxidizing agents, such as arsenic acid, stannic chloride, mercuric chloride, etc., several substances are formed, the principal of which are the two above named. Para-rosaniline, $C_{19}H_{17}N_3$, is formed from para-toluidine and aniline, according to the equation, —

$$\underset{\text{Aniline.}}{2\,C_6H_7N} + \underset{\text{Toluidine.}}{C_7H_9N} + 3\,O = \underset{\text{Para-rosaniline.}}{C_{19}H_{17}N_3} + 3\,H_2O.$$

Rosaniline, $C_{20}H_{19}N_3$, is formed in a similar way: —

$$\underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{Toluidine.}}{2\,C_7H_9N} + 3\,O = \underset{\text{Rosaniline.}}{C_{20}H_{19}N_3} + 3\,H_2O.$$

The composition and modes of formation of the two substances show that rosaniline is a homologue of para-rosaniline, the relation between the two substances being represented by the formulas $C_{19}H_{17}N_3$ and $C_{19}H_{16}(CH_3)N_3$.

By treating para-rosaniline with a reducing agent, it is converted into para-leucaniline, which has been shown to be triamido-triphenyl-methane: —

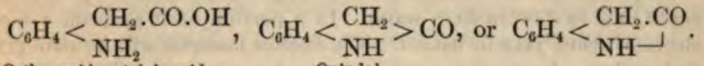
$$\underset{\text{Para-rosaniline.}}{C_{19}H_{17}N_3} + H_2 = \underset{\text{Para-leucaniline.}}{C_{19}H_{19}N_3}\left( = C\left\{\begin{array}{l} C_6H_4 . NH_2 \\ C_6H_4 . NH_2 \\ C_6H_4 . NH_2 \\ H \end{array}\right.\right).$$

We see thus that para-rosaniline and rosaniline, which are the fundamental compounds of the group of aniline dyes, are derivatives of the hydrocarbon tri-phenyl-methane.

**Para-rosaniline, $C_{19}H_{17}N_3$.** — The formation of this substance by oxidation of para-leucaniline and of a mixture of toluidine and aniline was mentioned above. It is probably one of the constituents of the commercial dye known as *fuchsine*. The relation between para-rosaniline and para-leucaniline is probably expressed by the following formulas: —

$$\underset{\textit{Tri-phenyl-methane.}}{CH\left\{\begin{array}{l} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{array}\right.} \quad \underset{\text{Para-leucaniline.}}{CH\left\{\begin{array}{l} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \end{array}\right.} \quad \underset{\text{Triamido-triphenyl-carbinol.}}{C(OH)\left\{\begin{array}{l} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \end{array}\right.} \quad \underset{\text{Para-rosaniline.}}{C\left\{\begin{array}{l} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4 > \\ NH \end{array}\right.}.$$

According to this, para-rosaniline is an anhydride of triamido-triphenyl-carbinol, somewhat of the same order as oxindol, which is an anhydride of ortho-amido-α-toluic acid (see p. 293): —



$$C_6H_4<\begin{matrix}CH_2.CO.OH\\NH_2\end{matrix},\quad C_6H_4<\begin{matrix}CH_2\\NH\end{matrix}>CO, \text{ or } C_6H_4<\begin{matrix}CH_2.CO\\NH\text{—}\lrcorner\end{matrix}.$$

Ortho-amido-α-toluic acid. Oxindol.

**Rosaniline, $C_{20}H_{19}N_3$.** — This is the principal constituent of commercial fuchsine. It is formed by oxidizing a mixture of aniline and toluidine: —

$$C_6H_7N + 2\,C_7H_9N + 3\,O = C_{20}H_{19}N_3 + 3\,H_2O.$$

**Experiment 78.** In a dry test-tube put a little dry mercuric chloride and a few drops of commercial aniline. Heat over a small flame. Dissolve the product in alcohol, with the addition of a little hydrochloric or acetic acid. The beautiful color of the solution is due to the presence of the hydrochloride or acetate of rosaniline.

On the large scale, the oxidizing agent used is arsenic acid. Care is taken to remove all arsenic acid from the product, but it is nevertheless sometimes found in the products obtained in the market. Rosaniline crystallizes in needles or plates. It is very slightly soluble in water; more readily soluble in alcohol. It forms three series of salts with monobasic acids. With hydrochloric acid it forms the salts $C_{20}H_{19}N_3.HCl$ and $C_{20}H_{19}N_3.3\,HCl$. The former is the substance known as *fuchsine*, though some of the fuchsine met with in the market is the acetate of rosaniline, $C_{20}H_{19}N_3.C_2H_4O_2$. Fuchsine and the other salts of rosaniline dye wool and silk directly. For dyeing cotton cloth, however, a *mordant* is necessary.

*Dyeing.* Animal fibres, in general, are colored directly by dyes; that is to say, they have the power of forming with the dyes stable compounds which adhere to the fibres. This is not true of vegetable fibres, as cotton cloth and linen. Hence, in order to dye the latter, something must be added of such a character that, with the dye, it forms a compound which adheres to the fibres. Substances which act in this way are called *mordants.* Among the substances used as mordants are aluminium acetate, ferric acetate, and some salts of tin.

**Experiment 79.** Make a dilute solution of picric acid by dissolving $2^g$ to $3^g$ in $200^{cc}$ to $300^{cc}$ water. In a portion of it suspend a few pieces of white yarn or flannel. The *woollen* material will be strongly died yellow. In another portion suspend a piece of ordinary cotton cloth. And in a third portion introduce a piece of cotton cloth which has been soaked in aluminium acetate and afterwards partly dried. The aluminium acetate may be made by treating a solution of sugar of lead with enough of a solution of alum to precipitate the lead, and then filtering off the lead sulphate. The unprepared cotton cloth, when removed from the picric acid solution and washed, will be found to be only slightly colored; whereas, that piece which was soaked in the mordant will be found to be strongly dyed. Similar experiments may be made with fuchsine.

Among the simpler aniline dyes are the following: —

*Hofmann's Violet.* This is either the hydrochloric acid or acetic acid salt of tri-methyl-rosaniline. It is made by heating together a salt of rosaniline, methyl iodide, methyl alcohol, and caustic potash.

*Iodine Green* is the iodide of penta-methyl-rosaniline.

*Aniline Blue* is tri-phenyl-rosaniline, $C_{20}H_{16}(C_6H_5)_3N_3$, which is formed by heating salts of rosaniline with an excess of aniline.

## PHTHALEÏNS.

In speaking of phthalic anhydride, it was stated that when this substance is treated with phenols, phthaleïns are formed; and, in speaking of resorcin, a markedly fluorescent body was mentioned as being formed when phthalic acid and resorcin are heated together.

**Phenol-phthaleïn, $C_{20}H_{14}O_4$.** — This substance is formed by treating a mixture of phenol and phthalic anyhdride with sulphuric acid or some other dehydrating agent: —

$$\underset{\text{Phenol.}}{2\,C_6H_6O} + \underset{\text{Phthalic anhydride.}}{C_8H_4O_3} = \underset{\text{Phenol-phthaleïn.}}{C_{20}H_{14}O_4} + H_2O.$$

The fused mass is dissolved in caustic soda, and the phenol-phthaleïn precipitated by the addition of an acid. It forms a granular crystalline powder. Its solution in alkalies is red or violet, according to the thickness of the layer. Acids destroy the color. Hence it is used as an indicator in alkalimetry as a substitute for litmus.

Phenol-phthaleïn, like rosaniline, is a derivative of tri-phenyl-methane, as has been shown by the following somewhat complicated reactions: —

The chloride of phthalic acid, or phthalyl chloride, $C_8H_4O_2Cl_2$, when treated with benzene in the presence of aluminium chloride, gives up its two atoms of chlorine, and in their place takes up two phenyl groups, thus: —

$$\underset{\text{Phthalyl chloride.}}{C_8H_4O_2Cl_2} + 2\,C_6H_6 = \underset{\text{Diphenyl-phthalide.}}{C_8H_4O_2(C_6H_5)_2} + 2\,HCl.$$

The substance thus formed is known as *diphenyl-phthalide*. Its conduct towards water and bases is such as to show that it is the anhydride of an acid: —

$$C_8H_4O_2(C_6H_5)_2 + H_2O = C_8H_6O_3(C_6H_5)_2$$
$$\text{or } C_7H_5O\left\{\begin{array}{l} CO_2H \\ (C_6H_5)_2 \end{array}\right..$$

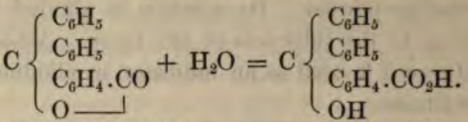
When this acid is reduced by means of zinc dust it loses oxygen: —

$$C_7H_5O\left\{\begin{array}{l} CO_2H \\ (C_6H_5)_2 \end{array}\right. = C_7H_5\left\{\begin{array}{l} CO_2H \\ (C_6H_5)_2 \end{array}\right. + O.$$

And, finally, when the last product is distilled with baryta, it loses carbon dioxide and yields tri-phenyl-methane: —

$$C_7H_5\left\{\begin{array}{l} CO_2H \\ (C_6H_5)_2 \end{array}\right. = CH\left\{\begin{array}{l} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{array}\right. + CO_2.$$

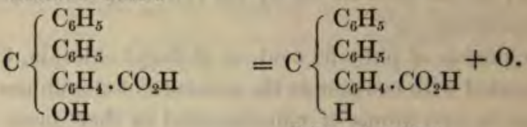
We have thus passed from phthalic anhydride to tri-phenyl-methane, and the reactions just referred to are in all probability correctly represented by the following formulas and equations:—



$$C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_4.CO\\O\text{——}\rfloor\end{array}\right. + H_2O = C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_4.CO_2H.\\OH\end{array}\right.$$

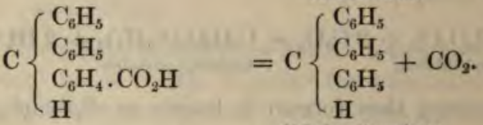
Diphenyl-phthalide, or anhydride of triphenyl-carbinol-carbonic acid.

Triphenyl-carbinol-carbonic acid.



$$C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_4.CO_2H\\OH\end{array}\right. = C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_4.CO_2H\\H\end{array}\right. + O.$$

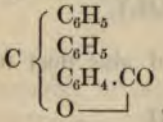
Triphenyl-methane-carbonic acid.

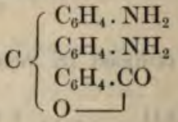


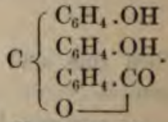
$$C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_4.CO_2H\\H\end{array}\right. = C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_5\\H\end{array}\right. + CO_2.$$

Tri-phenyl-methane.

Now, by making dinitro-diphenyl-phthalide, reducing it, and boiling the diazo compound with water, the product is phenol-phthaleïn. Hence, the latter compound appears to be the dihydroxy derivative of diphenyl-phthalide:—



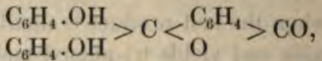




$$C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_4.CO\\O\text{——}\rfloor\end{array}\right. \qquad C\left\{\begin{array}{l}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.CO\\O\text{——}\rfloor\end{array}\right. \qquad C\left\{\begin{array}{l}C_6H_4.OH\\C_6H_4.OH.\\C_6H_4.CO\\O\text{——}\rfloor\end{array}\right.$$

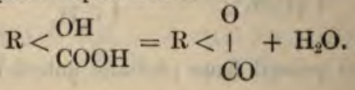
Phenol-phthaleïn.

The formula for phenol-phthaleïn may also be written thus:—



$$\begin{array}{l}C_6H_4.OH\\C_6H_4.OH\end{array}\!\!>C<\!\!\begin{array}{l}C_6H_4\\O\end{array}\!\!>CO,$$

the curious arrangement of the carbonyl group being simply the sign of the anhydride condition between carboxyl and hydroxyl, of which the simplest expression is



$$R<\begin{array}{l}OH\\COOH\end{array} = R<\begin{array}{c}O\\|\\CO\end{array} + H_2O.$$

NOTE FOR STUDENT. — Although the reactions above briefly described may at first sight appear to be difficult to comprehend, they are in reality simple enough. The student is earnestly recommended not to slight them on account of the long names and complex formulas involved. They afford an excellent example of the methods upon which we rely for determining the nature of complex substances. Notice that all appears dark until the well-known substance tri-phenyl-methane is obtained, which suggests that all the substances are derivatives of this fundamental hydrocarbon; and how easily, when this conception has once been formed, the interpretation of all the reactions follows.

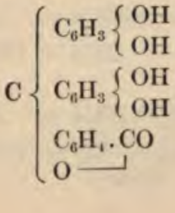
Among the other phthaleïns which deserve special mention is that which is formed with resorcin.

**Fluoresceïn, resorcin-phthaleïn, $C_{20}H_{12}O_5$.** — This beautiful substance is formed by simply heating together resorcin and phthalic anhydride: —

$$2\,C_6H_4(OH)_2 + C_8H_4O_3 = C_{20}H_{12}O_5 + 2\,H_2O.$$

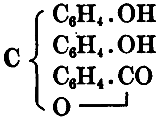
Its solutions in alkalies are wonderfully fluorescent. The substance, which is sold under the name "*uranin*" for the purpose of exhibiting the phenomenon of fluorescence, is an alkaline salt of fluoresceïn.

The reaction which takes place between resorcin and phthalic anhydride, when fluoresceïn is formed, is of the same kind as that which takes place between phenol and the anhydride to form phenol-phthaleïn. We would therefore expect to find that fluoresceïn is expressed by the formula



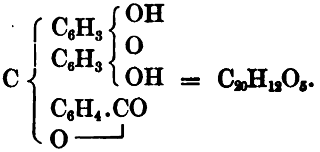
$$C\left\{\begin{array}{l} C_6H_3\left\{\begin{array}{l}OH\\ OH\end{array}\right. \\ C_6H_3\left\{\begin{array}{l}OH\\ OH\end{array}\right. \\ C_6H_4\,.\,CO \\ O\text{——}\lrcorner \end{array}\right.$$

which shows its analogy to phenol-phthaleïn,



$$C\begin{cases}C_6H_4.OH\\C_6H_4.OH\\C_6H_4.CO\\O\end{cases}$$

It is found, however, that in reality fluoresceïn corresponds to the above formula less one molecule of water; and it is believed that the water is given off as represented thus: —



$$C\begin{cases}\begin{matrix}C_6H_3\\C_6H_3\end{matrix}\left\{\begin{matrix}OH\\O\\OH\end{matrix}\right.\\C_6H_4.CO\\O\end{cases} = C_{20}H_{12}O_5.$$

Fluoresceïn.

**Eosin, tetra-brom-fluoresceïn, $C_{20}H_8Br_4O_5$,** is formed by treating fluoresceïn with bromine. Its dilute solutions have an exquisite, delicate pink color which suggests a color often seen in the sky at the dawn of day. Hence the name ***eosin***, from ἠώς, *dawn*. It is fluorescent, and is used as a dye.

# CHAPTER XVII.

## HYDROCARBONS, $C_nH_{2n-8}$, AND DERIVATIVES.

THE hydrocarbons thus far considered are of three classes. They are: (1) paraffins, or saturated hydrocarbons of the marsh-gas series; (2) unsaturated hydrocarbons related to the paraffins; and (3) hydrocarbons which contain residues of the saturated paraffins and of benzene.

We now pass to a brief consideration of a hydrocarbon which is made up of a residue of benzene and of an unsaturated paraffin. It bears to ethylene the same relation that toluene bears to marsh gas; that is to say, it is phenyl-ethylene.

**Styrene, phenyl-ethylene,** $C_8H_8(=C_6H_5.CH.CH_2)$. — This hydrocarbon is contained in liquid storax, — a fragrant, honey-like substance which exudes from various plants, as the liquid-amber. It is formed by distilling cinnamic acid with lime: —

$$C_9H_8O_2 = C_8H_8 + CO_2.$$

NOTE FOR STUDENT. — What does this reaction suggest with regard to the relation between cinnamic acid and styrene?

It is also formed from phenyl-ethane, $C_6H_5.C_2H_5$, in the same way that ethylene is formed from ethane: —

$$\left\{\begin{array}{llll} C_2H_6 & + Br_2 & = C_2H_5Br & + HBr \\ C_2H_5Br & + KOH & = C_2H_4 & + KBr + H_2O \end{array}\right. ;$$

$$\begin{array}{llll} C_6H_5.C_2H_5 & + Br_2 & = C_6H_5.C_2H_4Br & + HBr; \\ C_6H_5.C_2H_4Br & + KOH & = \underset{\text{Styrene.}}{C_6H_5.C_2H_3} & + KBr + H_2O. \end{array}$$

Its formation by heating acetylene was mentioned on p. 223: —

$$4\,C_2H_2 = C_8H_8.$$

NOTE FOR STUDENT. — What other polymeric product is obtained by heating acetylene?

Styrene is a liquid of an aromatic odor; boils at 144° to 144.5°; insoluble in water; miscible with ether and alcohol in all proportions.

When heated alone up to 300°, or even when allowed to stand at ordinary temperatures, it is converted into a polymeric modification, called *meta-styrene*, which is a solid. This same change is readily effected by several reagents, such as iodine and concentrated sulphuric acid. Styrene unites directly with chlorine and bromine in the same way that ethylene does (see p. 212): —

$$C_6H_5.C_2H_3 + Br_2 = C_6H_5.C_2H_3Br_2.$$

Chromic acid and other oxidizing agents convert styrene into benzoic acid (see remarks, p. 246). Some higher members of this series have been prepared, such as *phenyl-propylene*, *phenyl-butylene*, etc.; but at present they are not of sufficient importance to make their consideration necessary.

Styrene is closely related to cinnamic acid, from which the interesting and important compounds of the indigo group are obtained.

**Styryl alcohol, $C_9H_{10}O(= C_6H_5.CH.CH.CH_2OH)$.** — This alcohol occurs in nature in the form of an ethereal salt of cinnamic acid in liquid storax, and also in balsam of Peru. It forms long, thin needles, which melt at 33°. It boils at 250°. It takes up hydrogen, and yields phenyl-propyl alcohol, $C_6H_5.CH_2.CH_2.CH_2OH$ (see p. 281): —

$$C_6H_5.CH.CH.CH_2OH + H_2 = C_6H_5.CH_2.CH_2.CH_2OH.$$

By treatment with hydriodic acid it yields allyl-benzene (*phenyl*-propylene), $C_6H_5.CH.CH.CH_3$, and toluene.

When oxidized with platinum black it is converted into the corresponding aldehyde, cinnamic aldehyde; and, by further oxidation, into cinnamic acid. The relations between the three substances are the familiar ones of a primary alcohol, and the corresponding aldehyde and acid: —

$$\underset{\text{Styryl alcohol.}}{C_6H_5.CH.CH.CH_2OH.} \qquad \underset{\text{Cinnamic aldehyde.}}{C_6H_5.CH.CH.CHO.}$$

$$\underset{\text{Cinnamic acid.}}{C_6H_5.CH.CH.CO_2H.}$$

These compounds are simply the phenyl derivatives of allyl alcohol, acroleïn, and acrylic acid: —

$$\underset{\text{Allyl alcohol.}}{CH_2.CH.CH_2OH.} \qquad \underset{\substack{\text{Acroleïn or} \\ \text{acrylic aldehyde.}}}{CH_2.CH.CHO.} \qquad \underset{\text{Acrylic acid.}}{CH_2.CH.CO_2H.}$$

**Cinnamic acid,**
**Phenyl-acrylic acid,** $\Big\}$ **$C_9H_8O_2(= C_6H_5.CH.CH.CO_2H)$.**

Cinnamic acid is found in liquid storax, partly in the free condition, and partly in the form of an ethereal salt in combination with styryl alcohol, as styryl cinnamate, in the balsams of Tolu and Peru. It may be made synthetically: —

1. By heating together benzoic aldehyde and acetyl chloride: —

$$C_6H_5.COH + CH_3.COCl = C_6H_5.C_2H_2.CO_2H + HCl.$$

This reaction will be better understood by writing it in two equations: —

$$(1)\ C_6H_5.CH\underline{\boxed{O} + C\boxed{H_2}}H.COCl = \underset{\text{Cinnamyl chloride.}}{C_6H_5.CH.CH.COCl} + H_2O;$$

$$(2)\ \underset{\text{Cinnamyl chloride.}}{C_6H_5.CH.CH.COCl} + H_2O = C_6H_5.CH.CH.CO_2H + HCl.$$

The kind of action represented in equation (1) is not uncommon. We have already met with it in the formation of mesitylene from acetone (see p. 248), in which case two hydrogens from each of three methyl groups unite with an oxygen atom from each of the three carbonyl groups. The product is called a *condensation-product*, and the action is known as condensation.

2. By heating together benzoic aldehyde and acetic anhydride: —

$$C_6H_5.COH + (C_2H_3O)_2O = C_6H_5.C_2H_2.CO_2H + C_2H_4O_2.$$

It is probable that the action between benzoic aldehyde and acetic anhydride is of the same kind as that between the aldehyde and acetyl chloride.

3. By treating benzal chloride with sodium acetate: —

$$C_6H_5.CH\underline{\boxed{Cl_2} + C\boxed{H_2}}H.CO_2Na = C_6H_5.CH.CH.CO_2Na + 2HCl.$$

$$C_6H_5.CH.CH.CO_2Na + HCl = C_6H_5.CH.CH.CO_2H + NaCl.$$

The acid is now manufactured on the large scale by this last method.

Cinnamic acid is a solid which crystallizes in monoclinic prisms. It melts at 133°, and boils at 300° to 304°. It is easily broken up into styrene and carbon dioxide: —

$$C_6H_5.CH.CH.CO_2H = C_6H_5.CH.CH_2 + CO_2.$$

Oxidizing agents convert it first into benzoic aldehyde and then into benzoic acid. Nascent hydrogen converts it into hydro-cinnamic or phenyl-propionic acid, $C_6H_5.CH_2.CH_2.CO_2H$ (p. 293). It unites with hydrochloric, hydrobromic, and hydriodic acids: —

$$C_6H_5.C_2H_2.CO_2H + HCl = \underset{\text{Phenyl-chlor-propionic acid.}}{C_6H_5.C_2H_3Cl.CO_2H.}$$

Treated with substituting agents, such as nitric acid, etc., it yields substitution-products in which the entering atoms or groups are contained in the benzene residue, in the ortho and para positions relatively to the acrylic acid residue, $C_2H_2.CO_2H$. *Bromine* yields the addition-product $C_6H_5.C_2H_2Br_2.CO_2H$.

**Nitro-cinnamic acids,** $C_6H_4\left\{\begin{matrix}C_2H_2.CO_2H\\NO_2\end{matrix}\right.$. — The ortho- and para-acids are formed by dissolving cinnamic acid in nitric acid.

NOTE FOR STUDENT. — What are the products when toluene is treated with nitric acid? When benzoic acid is treated in the same way? To which case is the above analogous?

**Amido-cinnamic acids,** $C_6H_4\left\{\begin{matrix}C_2H_2.CO_2H\\NH_2\end{matrix}\right.$. — These acids are formed by treating the nitro-acids with reducing agents. The ortho-acid loses water when set free from its salts, and forms the anhydride *carbostyril*, $C_6H_4 < \begin{matrix}C_2H_2\\N\end{matrix} \geqslant C.OH$, analogous to hydro-carbostyril (p. 294).

**Coumarin,** $C_9H_6O_2\left(=C_6H_4\left\{\begin{matrix}C_2H_2CO\\O\end{matrix}\right.\right)$, is a compound found in Tonka beans, and in some other plant-substances. It has been made synthetically from salicylic aldehyde and acetic anhydride, just as cinnamic acid is made from benzoic aldehyde and acetic anhydride. The first product of this action is probably *ortho-hydroxy-cinnamic acid*, or coumaric acid, $C_6H_4\left\{\begin{matrix}C_2H_2.COOH\\OH(o)\end{matrix}\right.$, which then loses water, yielding the anhydride or coumarin. Coumarin has a pleasant odor, like that of vanillin, and is used for flavoring. Treated with bases, it yields salts of coumaric acid.

# CHAPTER XVIII.

## PHENYL-ACETYLENE AND DERIVATIVES.

**Phenyl-acetylene, acetenyl-benzene, $C_6H_5.C.CH$,** bears to acetylene the same relation that styrene, or phenyl-ethylene, bears to ethylene. It is made from styrene in the same way that acetylene is made from ethylene: —

$$\begin{array}{lllll}(1) & C_2H_4 & + Br_2 & = C_2H_4Br_2; & \\ (2) & C_2H_4Br_2 & + 2\,KOH & = C_2H_2 & + 2\,KBr + 2\,H_2O.\end{array}$$

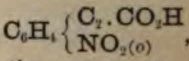
$$\begin{array}{llll} C_6H_5.C_2H_3 & + Br_2 & = C_6H_5.C_2H_3Br_2; & \\ C_6H_5.C_2H_3Br_2 & + 2\,KOH & = \underset{\text{Phenyl-acetylene.}}{C_6H_5.C_2H} & + 2\,KBr + 2\,H_2O.\end{array}$$

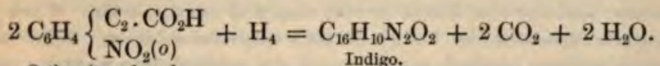
It is a liquid which boils at 139° to 140°. It unites directly with four atoms of bromine, forms metallic derivatives, and, in general, conducts itself like acetylene (which see).

**Phenyl-propiolic acid, $C_9H_6O_2(= C_6H_5.C.C.CO_2H)$.**—This acid is a carboxyl derivative of phenyl-acetylene, bearing to it the same relation that cinnamic acid bears to phenyl-ethylene. It is made from cinnamic acid, by treating brom-cinnamic acid, $C_6H_5.C_2HBr.CO_2H$, with alcoholic potash: —

$$C_6H_5.C_2HBr.CO_2H = C_6H_5.C_2.CO_2H + HBr.$$

It forms long needles, which melt at 136° to 137°. When heated with water, it breaks up into carbon dioxide and phenyl-acetylene.

**Ortho-nitro-phenyl-propiolic acid,**  $C_6H_4\left\{\begin{matrix}C_2.CO_2H\\NO_{2(o)}\end{matrix}\right.$, is made from ortho-nitro-cinnamic acid, in the same way that *phenyl*-propiolic acid is made from cinnamic acid (see preceding paragraph). It is of special interest, for the reason that it can easily be transformed into indigo. The transformation is most readily effected by boiling it with alkalies and grape sugar, or some other mild reducing-agent. The reaction is represented by the following equation:—



$$2\,C_6H_4\left\{\begin{array}{l}C_2.CO_2H\\NO_2(o)\end{array}\right. + H_4 = C_{16}H_{10}N_2O_2 + 2\,CO_2 + 2\,H_2O.$$

Ortho-nitro-phenyl-propiolic acid. Indigo.

The acid is at present manufactured on the large scale, for the purpose of making indigo.

## INDIGO AND ALLIED COMPOUNDS.

In several plants, *Indigofera tinctoria*, *Isatis tinctoria*, etc., there occurs a glucoside called *indican*, which, under the influence of dilute mineral acids and certain ferments, breaks up, yielding indigo-blue and a substance resembling the glucoses. The indigo of commerce is prepared in the East and West Indies, in South America, Egypt, and other warm countries. At the proper stage the plants are cut off down to the ground, put in a large tank, and covered with water. Fermentation takes place, the indican breaking up and yielding indigo, as above stated. The liquid becomes green, and then blue. When the fermentation is finished, the liquid is drawn off into a second tank. This liquid contains the coloring-matter in solution. In contact with the air it is oxidized, forming indigo, which, being insoluble, is thrown down. In order to facilitate the precipitation of the indigo, the liquid is thoroughly stirred. Finally, the liquid is drawn off, the precipitated indigo pressed and dried, and then sent into the market.

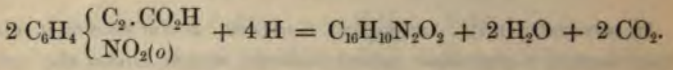
The substance prepared as above has a dark-blue color. It contains other coloring-matters besides indigo-blue. Its value depends upon the amount of the definite compound, indigo-blue, which it contains.

**Indigo-blue, indigotin, $C_{16}H_{10}N_2O_2$.** — Indigo-blue is obtained from commercial indigo by reducing it to indigo-white, and then exposing the clear colorless solution to the air, when indigo-blue is precipitated.

**Experiment 80.** Into a test-tube put a small quantity of powdered indigo; add fine zinc filings or zinc dust and caustic soda. When the mixture is heated the indigo forms a colorless solution. When this result has been reached, pour some of the solution into a small evaporating-dish. Contact with the air colors it blue.

Indigo-blue may be made artificially by a number of methods, among which the two following are the principal ones: —

1. By boiling ortho-nitro-phenyl-propiolic acid (which see) with an alkali and grape sugar: —



$$2\,C_6H_4\left\{\begin{matrix} C_2.CO_2H \\ NO_{2(o)} \end{matrix}\right. + 4\,H = C_{16}H_{10}N_2O_2 + 2\,H_2O + 2\,CO_2.$$

2. By heating isatine (which see) with phosphorus trichloride, phosphorus and acetyl chloride.

Without going into the mechanism of these reactions, we see that there are two general ways of obtaining indigo artificially. The first starts from cinnamic acid, which is successively converted into ortho-nitro-cinnamic acid and ortho-nitro-phenyl-propiolic acid; the second starts from benzoic acid, which is converted into ortho-nitro- and ortho-amido-benzoic acids. The latter is then converted successively into the chloride, cyanide, and corresponding acid, the anhydride of which is isatine. For fuller details of the reactions involved in the formation of ortho-nitro-phenyl-propiolic acid, see p. 328; and for similar details in regard to isatine, see p. 289. As has been stated, indigo is now manufactured on the large scale by the first of the two methods above given.

Indigo-blue crystallizes from aniline in dark-blue crystals. It sublimes in rhombic crystals. Its vapor has a purple-red color. It is insoluble in water, alcohol, and ether; soluble in *aniline* and chloroform. Oxidizing agents convert it into isatine (which see). Heated with solid caustic potash, it yields carbon dioxide and aniline; boiled with a solution of caustic potash and finely-powdered black oxide of manganese, it is converted into ortho-amido-benzoic acid (anthranilic acid) (see p. 289).

A great many compounds related to indigo have been made, of late years, incidentally to the study of its chemical conduct. The synthesis of indigo has been effected, as a result of this study. The work undertaken was suggested by the few fundamental facts, above stated, that indigo when decomposed readily yields aniline and ortho-amido-benzoic acid. The question which investigators have endeavored to answer is, What relations do indigo-blue and the compounds allied to it bear to ortho-amido-benzoic acid? Although, as far as indigo-blue is concerned, this has proved to be a difficult question, to which a definite answer is still lacking, as far as some of the simpler derivatives are concerned it has been answered. Two of these, oxindol and isatine, have been considered in connection with the simpler compounds, to which they are most closely related. A few others will here be mentioned.

**Indigo-white, $C_{16}H_{12}N_2O_2$,** is formed by reduction of indigo-blue, as above described. Its solutions rapidly turn blue in the air, in consequence of the formation of indigo-blue.

When indigo is oxidized with nitric acid, isatine, $C_8H_5NO_2$, is formed: —

$$C_{16}H_{10}N_2O_2 + O_2 = 2\,C_8H_5NO_2.$$

When isatine is treated with sodium amalgam, it takes up hydrogen, and yields *dioxindol*, $C_8H_7NO_2$: —

$$\underset{\text{Isatine.}}{C_8H_5NO_2} + H_2 = \underset{\text{Dioxindol.}}{C_8H_7NO_2}.$$

By further reduction, dioxindol loses an atom of oxygen, yielding *oxindol*, $C_8H_7NO$: —

$$\underset{\text{Dioxindol.}}{C_8H_7NO_2} + H_2 = \underset{\text{Oxindol.}}{C_8H_7NO} + H_2O.$$

The relations between oxindol and isatine cannot readily be made clear without a careful study of some very complex reactions.

It would also lead too far and be unprofitable to discuss here the constitution of indigo-blue itself. Suffice it to say, that it has been shown to consist of a doubled group very similar to that of oxindol.

# CHAPTER XIX.

## HYDROCARBONS CONTAINING TWO BENZENE RESIDUES IN DIRECT COMBINATION.

JUST as the marsh-gas residue, methyl, $CH_3$, unites with methyl to form ethane, $\begin{matrix}CH_3\\ |\\ CH_3\end{matrix}$, so the benzene residue, phenyl, $C_6H_5$, unites with phenyl to form the hydrocarbon, diphenyl, $\begin{matrix}C_6H_5\\ |\\ C_6H_5\end{matrix}$, and similar residues of toluene, and the higher members of the series unite in a similar way to form homologues of diphenyl.

**Diphenyl, $C_{12}H_{10}(=C_6H_5.C_6H_5)$.**—This hydrocarbon is made by treating brom-benzene with sodium:—

$$2\,C_6H_5Br + 2\,Na = C_{12}H_{10} + 2\,NaBr;$$

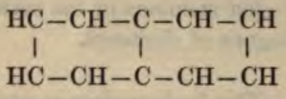
and by conducting benzene through a tube heated to redness:—

$$2\,C_6H_6 = C_{12}H_{10} + H_2.$$

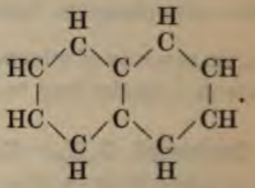
It forms large, lustrous plates. It melts at 70.5°, and boils at 254°. It is easily soluble in hot alcohol and ether.

Diphenyl is an extremely stable substance. It resists the action of ordinary oxidizing agents, but with strong ones it yields benzoic acid. A large number of derivatives of diphenyl have been studied. A curious one, known as *carbazol*, occurs in coal tar. This has been shown to be a substituted ammonia containing a residue of diphenyl. It is properly designated by the name *diphenyl-imide*, and is represented by the formula $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>NH$. It has been made synthetically by passing the vapor of diphenyl amine, $NH\left\{\begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\right.$, through a red-hot tube, a reaction taking place which is analogous to that mentioned above as taking place when benzene is treated in the same way, the product in the latter case being diphenyl.

**Naphthalene, $C_{10}H_8$.** — While the relations of diphenyl to benzene are clearly shown by its simple synthesis from brombenzene, the relations of naphthalene to benzene have been discovered through a careful study of its chemical conduct. The facts can be best interpreted by assuming that the molecule of naphthalene is formed by the union of two benzene residues in such a way that they have two carbon atoms in common, as represented in the formulas



and



How this conception was formed will be shown below, after the properties and the reactions of naphthalene shall have been considered.

Naphthalene is a frequent product of the heating of organic substances. Thus, it is formed by passing the vapors of alcohol, ether, acetic acid, volatile oils, petroleum, benzene, toluene, etc., through red-hot tubes; and, also, by treating ethylene and acetylene in the same way. It is therefore found in coal tar, and is sometimes found in gas-pipes used for gas made by heating naphtha, gasoline, etc., to high temperatures. It has been made synthetically by conducting phenyl-butylene bromide over highly-heated lime: —

$$C_6H_5.C_4H_7Br_2 = C_4H_4.C_2.C_4H_4 + H_2 + 2\,HBr;$$

and by conducting isobutyl-benzene over lead oxide: —

$$C_6H_5.C_4H_9 + O_3 = C_4H_4.C_2.C_4H_4 + 3\,H_2O.$$

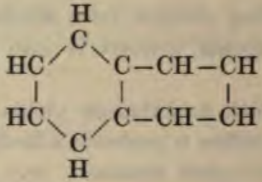
Neither of these reactions, however, is of much assistance in enabling us to form a conception in regard to the nature of naphthalene.

Naphthalene is prepared on the large scale from those portions of coal tar which boil between 180° to 220°. This material is treated with caustic soda, and then with sulphuric acid, and distilled with water vapor.

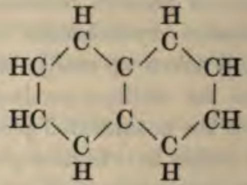
It forms colorless, lustrous, monoclinic plates. It melts at 79.2°, and boils at 216.6°. It has a pleasant odor; is volatile with water vapor, and sublimes readily. It is insoluble in water; easily soluble in boiling alcohol, from which it may be crystallized. Oxidizing agents convert it into phthalic acid (see Exp. 74).

The ease with which naphthalene yields phthalic acid, suggests that the hydrocarbon is probably a di-derivative of benzene containing two hydrocarbon residues; such, for example, as is represented by the formula $C_6H_4\left\{\begin{matrix}C_2H_2\\C_2H_2\end{matrix}\right.$. Such a substance, however, contains unsaturated paraffin residues, and hence ought readily to take up bromine, hydrobromic acid, etc. Bromine and chlorine are indeed taken up easily, but the products thus obtained act rather like the addition-products of benzene than the addition-products of the unsaturated paraffins. They break up readily, and yield stable substitution-products of naphthalene; and, further, the first product of the action of bromine on naphthalene is not an addition-product, but mono-brom-naphthalene, $C_{10}H_7Br$, a fact which shows that substitution takes place more easily with naphthalene than addition. We have seen that a hydrocarbon containing a benzene residue and an unsaturated paraffin residue, as, for example, styrene or phenyl-ethylene, $C_6H_5.C_2H_3$, and phenyl-acetylene, $C_6H_5.C_2H$, when treated with bromine or hydrobromic acid, takes them up as readily as ethylene and acetylene, and this action takes place before substitution. According to this, naphthalene ought to take up bromine with avidity before substitution of its hydrogen takes place.

The formula $C_6H_4\left\{\begin{matrix}C_2H_2\\C_2H_2\end{matrix}\right.$ and similar ones being thus rendered extremely improbable, the next thought that suggests itself is that the two groups $C_2H_2$ may be united, as represented in the formula $C_6H_4\left\{\begin{matrix}CH.CH\\|\\CH.CH\end{matrix}\right.$. Assuming, further, that the two groups are united to two carbon atoms of the benzene residue which are in the ortho relation to each other, we may write this same formula thus: —

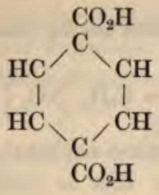


or, what is the same thing, —

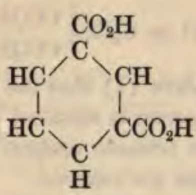


This formula represents naphthalene as made up of two benzene residues united in such a way that they have two carbon atoms in common. This, as has been stated, represents the hypothesis at present held in regard to the nature of naphthalene.

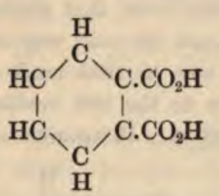
As regards the assumption that the two residues are united through carbon atoms which are in the ortho position relatively to each other, it should be said that this assumption is made because phthalic acid is the product of oxidation; and the facts already considered have shown us that terephthalic acid must be represented by the formula



and isophthalic acid by



and hence, in terms of the accepted hypothesis, the third possible formula must be given to phthalic acid; viz., —



Are there any facts besides the few above mentioned which make the hypothesis appear probable?

There is an ingenious and interesting line of reasoning which appears to show that the fundamental notion involved in the above formula for naphthalene is true. This fundamental notion is that the hydrocarbon consists of two benzene residues which have two carbon atoms in common. The facts which lead to this conclusion are the following: —

When nitro-naphthalene is oxidized it yields nitro-phthalic acid. This shows that the nitro group is contained in a benzene residue; and we may represent it by the formula

$C_6H_3.NO_2\left\{\begin{matrix}C_2H_2\\C_2H_2\end{matrix}\right.$, the oxidation taking place as indicated thus:—

$$C_6H_3.NO_2\left\{\begin{matrix}C_2H_2\\C_2H_2\end{matrix}\right. + 9\,O = C_6H_3.NO_2\left\{\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. + H_2O + 2\,CO_2.$$

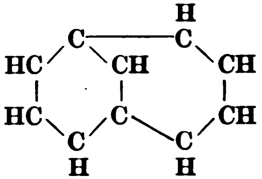
By reducing this same nitro-naphthalene, amido-naphthalene is obtained; and, when this is oxidized, phthalic acid is formed: —

$$C_6H_4\left\{\begin{matrix}C_2H.NH_2\\C_2H_2\end{matrix}\right. + 9\,O = C_6H_4\left\{\begin{matrix}CO_2H\\CO_2H\end{matrix}\right. + 2\,CO_2 + HNO_3.$$

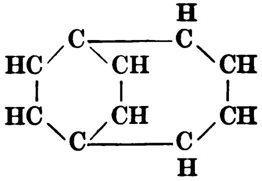
These two reactions show (1) that the part of nitro-naphthalene in which the nitro group is situated is a benzene residue; (2) that there is another benzene residue in the compound into which the nitro group has not entered.

It has been noticed, also, that by oxidation of a naphthalene-sulphonic acid, both sulpho-phthalic and phthalic acid itself are obtained.

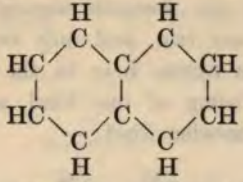
It follows, from these facts, that naphthalene is made up of two benzene residues, and the only way in which a hydrocarbon of the formula $C_{10}H_8$ can be thus made up, is by having two carbon atoms common to the two residues, as represented in the formula already given. It cannot be made up thus: —



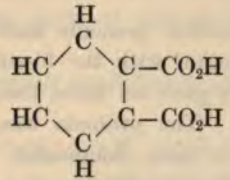
nor thus : —



for neither of these formulas expresses the fundamental idea of the presence of two benzene residues in the same molecule. The only formula which expresses this idea in terms of the commonly accepted hypothesis for benzene is



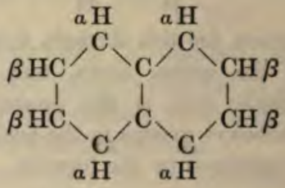
The proof just given for this formula is independent of any notions regarding the ortho, meta, and para relations in benzene. As phthalic acid is the product of oxidation, it follows that the carboxyl groups in the acid must bear to each other the relation expressed by the formula



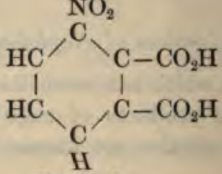
and, therefore, that in all ortho compounds the substituting groups bear this same relation to each other. Hence, by starting with the notion that the above formula represents phthalic acid,—and to this notion, it must be remembered, we are led independently of any facts connected with the formation of the acid from naphthalene,—the accepted formula of naphthalene follows naturally. And, on the other hand, we are led, by a study of naphthalene itself, to the accepted formula, and from this the above formula for phthalic acid follows.

### *Derivatives of Naphthalene.*

An interesting fact which has been discovered by a study of the mono-substitution products of naphthalene is this,—that two, and only two, varieties are known. There is an α- and a $\beta$-chlor-naphthalene, an $\alpha$- and a $\beta$-brom-naphthalene, etc., etc. This fact is quite in harmony with the views held regarding the constitution of naphthalene, as will readily be seen by examining the formula somewhat more in detail. We see that there are two, and only two, kinds of relations which the hydrogen atoms bear to the molecule; all those marked with an $\alpha$ being of one kind, and all those marked with a $\beta$ being of another kind:—

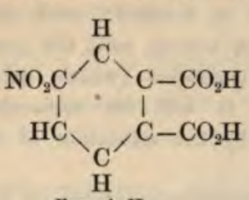


Here, again, a problem presents itself like that which was considered in connection with the bi-substitution products of benzene. Our theory gave us three formulas, and three compounds are known. The problem was, to determine which formula to assign to each compound. Here we have two formulas for two brom-naphthalenes and other mono-substitution products of naphthalene, and we actually have two compounds; and the question arises, which of the two formulas must we assign to a given compound? The method adopted is simple, and can be explained in a few words. That nitro derivative of naphthalene which is known as $\alpha$-nitro-naphthalene yields nitro-phthalic acid by oxidation; and the relation of the nitro group to the carboxyl groups, in this acid, has been determined. It is expressed by the formula



Formula I.

while the formula of the other nitro-phthalic acid is



Formula II.

As α-nitro-naphthalene yields the acid of formula I., it follows that in it the nitro group must occupy the position of one of the hydrogen atoms marked α in the above formula for naphthalene. Those substitution-products of naphthalene which belong to the same series as α-nitro-naphthalene are called α *derivatives*. In the β compounds the substituting group or atom must occupy the place of one of the hydrogen atoms marked β.

Among the derivatives of naphthalene are the following: —

**Naphthoïc acid, $C_{10}H_7.CO_2H$,** which bears to naphthalene the same relation that benzoic acid bears to benzene.

**α-Naphthol, $C_{10}H_7.OH$.** — This compound is made from naphthalene in the same way that phenol is made from benzene: —

1. By treating α-naphthyl-amine, $C_{10}H_7.NH_2$, with nitrous acid.

NOTE FOR STUDENT. — Write the equations.

2. By melting α-naphthalene-sulphonic acid with caustic potash.

NOTE FOR STUDENT. — Write the equation.

α-Naphthol is a solid which melts at 96°. It has an odor somewhat resembling that of phenol. Its general chemical conduct is much like that of phenol. Toward oxidizing agents, however, its action is peculiar. Thus, when boiled with potassium chlorate and hydrochloric acid, a di-chlorine substitution-product is formed; and at the same time a second oxygen atom enters, and the product has the characteristics of the quinones (which see). It is di-chlor-naphtho-quinone. It will be remembered that ordinary quinone is formed by the oxidation of hydro-quinone, a di-hydroxyl derivative.

Some of the substitution-products of naphthol are used as dyes; as, for example, *dinitro-naphthol*, $C_{10}H_5(NO_2)_2OH$, which is known as *Martius's Yellow; dinitro-naphthol-sulphonic acid*, $C_{10}H_4(NO_2)_2(SO_3H).OH$, the potassium salt of which, $K_2C_{10}H_4N_2SO_8$, is known as *Naphthol Yellow S.* With diazo compounds, naphthol has a remarkable power of combination; and a great many derivatives containing residues of diazo compounds, and of naphthol or its substitution-products, have been made, and some of them have found application as dyes. The simplest compound of this kind is formed by bringing together naphthol and diazo-benzene nitrate:—

$$C_{10}H_7.OH + C_6H_5{-}N_2{-}NO_3 = C_{10}H_6\left\{\begin{array}{l}N_2{-}C_6H_5\\ OH\end{array}\right. + HNO_3.$$

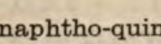
It is called *naphthol-diazo-benzene.* The dye known as *Poirrier's Orange II.* is a sulphonic acid of naphthol-diazo-benzene, and is probably formed by treating diazo-benzene-sulphonic acid with naphthol.

**Naphtho-quinone, $C_{10}H_6O_2$.**—This compound is obtained by oxidizing naphthalene with chromic acid; also by oxidizing $\alpha$-amido-$\alpha$-naphthol and other di-substitution products of naphthalene in which the two substituting groups are in the para position relatively to each other. It bears to naphthalene the same relation that ordinary quinone bears to benzene; that is, it is naphthalene in which two hydrogen atoms are replaced by two oxygen atoms.

It forms yellow needles, which melt at 125°. Like ordinary quinone, it is volatile with water vapor. Hydriodic acid converts it into *hydro-napthō-quinone:* —

$$C_{10}H_6O_2 + H_2 = C_{10}H_6(OH)_2.$$

Note for Student. — Compare with the action of reducing agents on ordinary quinone.



**Di-hydroxy-naphtho-quinone,** $C_{10}H_4\left\{\begin{matrix}(OH)_2\\O_2\end{matrix}\right.$, is a dye known by the name *naphthazarin*, on account of its resemblance to *alizarin* (which see).

Two homologues of naphthalene — methyl- and ethyl-naphthalene — have been prepared. β-Methyl-naphthalene has been found in coal tar.

## Quinoline and Analogous Compounds.

It has been stated, that, by distilling quinine and cinchonine with caustic potash, pyridine and some of its homologues are obtained. At the same time a base belonging to another series is formed, together with some of its homologues. This base is known as *quinoline*, to suggest its formation from quinine. It has the composition expressed by the formula $C_9H_7N$. The next two homologues of quinoline are lepidine, $C_{10}H_9N$, and dispoline, $C_{11}H_{11}N$. Three bases, isomeric with the three named, have been found in coal tar. These are known as leucoline, iridoline, and cryptidine. We thus have the two series: —

| BASES FROM ALKALOIDS. | | BASES FROM COAL TAR. |
|---|---|---|
| Quinoline . . . | $C_9H_7N$ . . . | Leucoline. |
| Lepidine . . . | $C_{10}H_9N$ . . . | Iridoline. |
| Dispoline . . . | $C_{11}H_{11}N$ . . . | Cryptidine. |

**Quinoline,** $C_9H_7N$. — Quinoline is formed by the distillation of quinine, cinchonine, or strychnine, with caustic potash. It is formed from certain derivatives of benzene.

1. By passing allyl-aniline over heated lead-oxide:—

$$C_6H_5.NH.C_3H_5 = C_9H_7N + 4\,H.$$

2. By heating together glycerin, aniline, and nitro-benzene:—

(1) $C_6H_5.NO_2 + C_3H_8O_3 = C_9H_7N + 3\,H_2O + O_2$;

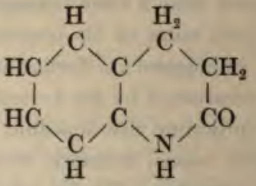
(2) $C_6H_5NH_2 + C_3H_8O_3 = C_9H_7N + 3\,H_2O + H_2$;

(3) $2\,C_6H_5NH_2 + C_6H_5NO_2 + 3\,C_3H_8O_3 = 3\,C_9H_7N + 11\,H_2O$.

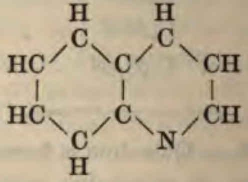
3. From di-chlor-quinoline:—

$$C_9H_5Cl_2N + 4\,H = C_9H_7N + 2\,HCl.$$

The last method is the most suggestive, as it leads to a definite view in regard to the relation between quinoline and benzene. Di-chlor-quinoline is made by treating hydro-carbostyril with phosphorus pentachloride. Hydro-carbostyril is the anhydride of ortho-hydro-cinnamic acid. This relation is partly expressed by the formula:—



The transformation of hydro-carbostyril into di-chlor-quinoline takes place easily; and the reaction can be best interpreted by assuming quinoline to be made up thus:—



*Quinoline* is thus regarded as formed from the union of a residue of benzene and a residue of pyridine, in the same way that naphthalene is believed to be formed from two residues of benzene. The formula suggests the existence of two isomeric quinolines, in one of which the nitrogen is in the $\alpha$ position, as represented in the above formula, while in the other it is in the $\beta$ position. The bases from the alkaloids belong to the $\alpha$ series; those from coal tar belong to the $\beta$ series.

Quinoline is a liquid which boils at 237°. Potassium permanganate converts it partially into cinchomeronic acid, $C_7H_5NO_4$. This is a *pyridine-dicarbonic acid*, $C_5H_3N(CO_2H)_2$. The formation of this acid is analogous to that of phthalic acid formed by oxidizing naphthalene.

Quinoline readily takes up hydrogen, forming *hydro-quinoline*, $C_9H_9N$, and *tetra-hydro-quinoline*, $C_9H_{11}N$. These, as well as the hydrogen addition-products of pyridine, are believed to exist in the alkaloids. Tetra-hydro-quinoline has been found in the crude quinoline obtained by distilling cinchonine with caustic soda.

Many derivatives of quinoline have been made. Substitution-products are obtained by treating nitro-products of substituted benzene with glycerin and aniline.

A sulphonic acid is obtained by treatment of quinoline with sulphuric acid. From this, *hydroxy-quinoline*, $C_9H_6(OH)N$, has been obtained. Hydroxy-quinoline, like quinoline itself, takes up hydrogen, forming *tetra-hydro-hydroxy-quinoline*, $C_9H_{10}.OH.N$. Finally, by treating this compound with methyl iodide, methyl is introduced, and a product obtained which is called *hydro-methoxy-quinoline*:—

$$C_9H_{11}ON + CH_3I = C_{10}H_{13}NO + HI.$$

This substance resembles quinine, and its hydrochloric acid salt is used in medicine to some extent as a substitute for quinine. The salt is known as *kairine*.

# CHAPTER XX.

## HYDROCARBONS CONTAINING TWO BENZENE RESIDUES INDIRECTLY COMBINED.

Diphenyl and naphthalene have been shown to consist of two benzene residues in direct combination. Diphenyl-methane is an example of a hydrocarbon consisting of two benzene residues in indirect combination, $C_6H_5 . CH_2 . C_6H_5$. As diphenyl-methane is closely related to toluene, it was considered in connection with the hydrocarbons of the benzene series. There are some hydrocarbons which have been shown to consist of two benzene residues united by means of residues of unsaturated paraffins. The most important of these is the well-known anthracene.

**Anthracene,** $C_{14}H_{10}$. — Anthracene is formed under conditions similar to those which give rise to the formation of naphthalene, especially by heating organic substances to a high temperature, and is hence found in coal tar.

It has been made synthetically from benzene derivatives by a number of methods: —

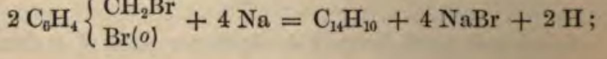
1. By passing benzyl-toluene, $C_6H_5 . CH_2 . C_6H_4 . CH_3$, over heated lead oxide: —

$$C_{14}H_{14} + 2\,O = C_{14}H_{10} + 2\,H_2O.$$

2. By heating benzyl-phenol with phosphorus pentoxide: —

$$2\,C_6H_5 . CH_2 . C_6H_4(OH) = C_{14}H_{10} + C_6H_6 + C_6H_5(OH) + H_2O.$$

3. By heating ortho-brom-benzyl bromide with sodium: —



$$2\,C_6H_4\left\{\begin{matrix} CH_2Br \\ Br(o) \end{matrix}\right. + 4\,Na = C_{14}H_{10} + 4\,NaBr + 2\,H;$$

or,

$$C_6H_4\left\{\begin{matrix}CH_2Br\\Br\end{matrix}\right. + \left.\begin{matrix}Br\\BrH_2C\end{matrix}\right\}C_6H_4 + 4\,Na$$

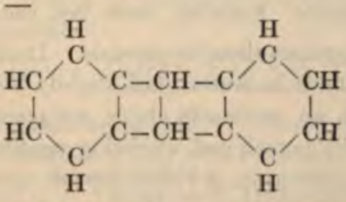
$$= C_6H_4\left\{\begin{matrix}CH\\CH\end{matrix}\right\}C_6H_4 + 4\,NaBr + 2\,H.$$

Anthracene is prepared in large quantity from those portions of coal tar which boil between 340° and 360°. The distillate is redistilled, and that which remains in the retort after the temperature has reached 350° is crystallized from xylene. It is then crystallized from alcohol, and finally sublimed. It is difficult to get it in perfectly pure condition. The color may be removed by dissolving the substance in benzene, and exposing it to direct sunlight. It forms laminæ, or monoclinic plates, which are fluorescent. It melts at 213°, and boils above 360°.

Anthracene takes up hydrogen, forming *di-hydro-anthracene*, $C_{14}H_{12}$, and *hexa-hydro-anthracene*, $C_{14}H_{16}$. It takes up bromine and chlorine, forming first addition-products, and then substitution-products.

Oxidizing agents convert anthracene into *anthra-quinone*, $C_{14}H_8O_2$, just as they convert naphthalene into naphtha-quinone.

The formation of anthracene from ortho-brom-benzyl-bromide (see above) furnishes strong proof in favor of the view that anthracene consists of two groups, $C_6H_4$, united by the group $C_2H_2$; thus, $C_6H_4.C_2H_2.C_6H_4$. It hence appears as a diphenylene[1] derivative of ethane, $C_2H_2(C_6H_4)_2$, analogous to diphenyl-ethane, $C_2H_4(C_6H_5)_2$. This conception may also be expressed thus:—



This is the formula commonly accepted for anthracene. It is in harmony with a large number of facts, and has been an efficient aid in investigations on anthracene and its derivatives.

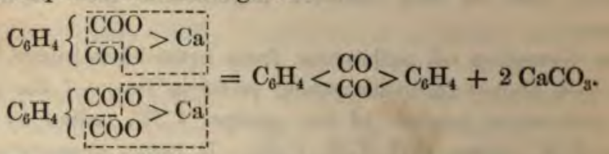
---

[1] Phenylene = $C_6H_4$.

**Anthraquinone,** $C_{14}H_8O_2 \left(= C_6H_4 < {CO \atop CO} > C_6H_4\right)$.—Anthraquinone is formed by direct oxidation of anthracene: —

$$C_{14}H_{10} + O_3 = C_{14}H_8O_2 + H_2O.$$

The simplest synthesis of anthraquinone that has been effected consists in distilling calcium phthalate. It is believed that the reaction which takes place is analogous to that which takes place when the calcium salt of a monobasic acid is distilled. As is well known, in the latter case a ketone containing one carbonyl group is formed; and it is believed that the product formed in the distillation of calcium phthalate contains two carbonyl groups, and that it is a representative of a class of bodies which may be called *diketones*. The subject of diketones was briefly discussed under the head of Quinones (which see). The equation representing the formation of anthraquinone from calcium phthalate is here given: —



$$\begin{matrix} C_6H_4 \left\{ {COO \atop CO.O} \right. > Ca \\ C_6H_4 \left\{ {CO.O \atop COO} \right. > Ca \end{matrix} = C_6H_4 < {CO \atop CO} > C_6H_4 + 2\,CaCO_3.$$

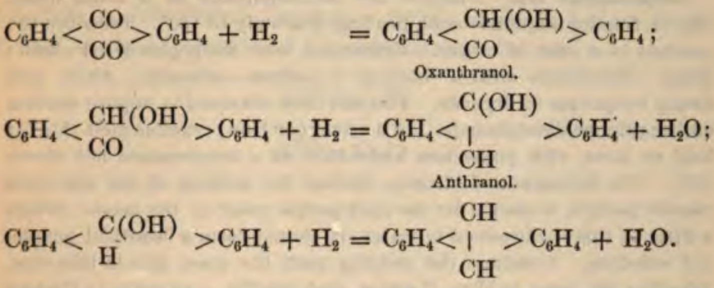
**Experiment 81.** Dissolve $10^g$ commercial anthracene in $50^{cc}$ to $75^{cc}$ glacial acetic acid. Add $20^g$ powdered potassium bichromate. Boil until the solution is dark green, and then add water. Anthraquinone is precipitated. Filter off, wash, dry, and sublime.

Anthraquinone forms rhombic crystals. It sublimes in yellow needles; is insoluble in water, but slightly soluble in alcohol and ether. It is an extremely stable compound, resisting the action of alcoholic potash and oxidizing agents. Melted with solid potassium hydroxide, it yields benzoic acid: —

$$C_{14}H_8O_2 \qquad + 2\,KOH = 2\,C_7H_5O_2K;$$

$$C_6H_4 < {CO \atop CO} > C_6H_4 + 2\,KOH = 2\,C_6H_5.COOK.$$

Reducing agents convert it successively into *oxanthranol*, $C_{14}H_{10}O_2$, *anthranol*, $C_{14}H_{10}O$, and *anthracene*, $C_{14}H_{10}$. These changes may be represented thus : —



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4 + H_2 = \underset{\text{Oxanthranol.}}{C_6H_4<\genfrac{}{}{0pt}{}{CH(OH)}{CO}>C_6H_4};$$

$$C_6H_4<\genfrac{}{}{0pt}{}{CH(OH)}{CO}>C_6H_4 + H_2 = \underset{\text{Anthranol.}}{C_6H_4<\begin{matrix}C(OH)\\ |\\ CH\end{matrix}>C_6H_4} + H_2O;$$

$$C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{H}>C_6H_4 + H_2 = C_6H_4<\begin{matrix}CH\\ |\\ CH\end{matrix}>C_6H_4 + H_2O.$$

When heated with zinc dust, it yields anthracene. A great many derivatives of anthraquinone have been made. Among the best known are the hydroxyl derivatives, some of which are much-prized dyes which are manufactured in great quantities.

The hydroxyl derivatives of anthraquinone may be made by melting either the bromine derivatives or the sulphonic acids with caustic potash.

**Alizarin,**
**Di-hydroxy-anthraquinone,** $\Big\}$ $C_{14}H_8O_4[=C_{14}H_6O_2(OH)_2]$.

Alizarin is the well-known dye which is obtained from madder root. The substance found in the root is *ruberythric acid*, a glucoside of the formula $C_{20}H_{22}O_{11}$. When this is treated with dilute acids or alkalies or ferments, it is decomposed, yielding alizarin and a glucose : —

$$C_{20}H_{22}O_{11} = \underset{\text{Alizarin.}}{C_{14}H_8O_4} + \underset{\text{Glucose.}}{C_6H_{12}O_6} + H_2O.$$

It is formed by melting dichlor- or dibrom-anthraquinone or anthraquinone-disulphonic acid with caustic potash : —

$$C_{14}H_6O_2(SO_3K)_2 + 2\,KOH = C_{14}H_6O_2(OH)_2 + 2\,K_2SO_3.$$

Alizarin is now manufactured from anthracene on the large scale, and large tracts of land which were formerly used for cultivating madder are now used for other purposes.

**Experiment 82.** Dissolve $20^{g}$ anthraquinone in a small quantity of fuming sulphuric acid, heating gradually to 160°. Dissolve the product in a litre of water. Neutralize with finely-powdered chalk; filter. Precipitate with a solution of sodium carbonate; filter; and finally evaporate to dryness. The salt thus obtained is impure sodium anthraquinone-disulphonate. In a silver (or iron) crucible melt this for half an hour, with potassium hydroxide, at a temperature not above 270°. The formation of alizarin, during the melting of the salt with caustic potash, is shown by the dark-purple color of the mass. When a little of this is dissolved in water, it should form a beautiful purple-red solution. Continue the melting until the mass acts in this way. Dissolve the mass in $\frac{3}{4}^{l}$ to $1^{l}$ water, and acidify. Alizarin is thrown down in brown amorphous flakes. Filter off, dry, and sublime between watch-glasses.

Alizarin forms red needles, which melt at 289° to 290°. It dissolves in alkalies, forming dark purple-red solutions. When heated with zinc dust, it yields anthracene. It was this reaction which gave the first clue to the nature of alizarin, and led, soon after, to its synthesis.

Some compounds, isomeric with alizarin, and also derived from anthracene, are known.

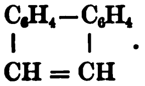
$$\left.\begin{array}{l}\textbf{Purpurin,}\\ \textbf{Tri-hydroxy-anthraquinone,}\end{array}\right\} C_{14}H_8O_5 = [C_{14}H_5O_2(OH)_3].$$

Purpurin is contained in madder root, and is therefore found in madder alizarin. It may be made by melting alizarin-sulphonic acid with caustic potash, and also by melting tri-brom-anthraquinone with caustic potash.

**Anthrapurpurin, isopurpurin,** $C_{14}H_5O_2(OH)_3$, is found in artificial alizarin.

---

**Phenanthrene,** $C_{14}H_{10}$, which is isomeric with anthracene, is also found in the higher boiling parts of coal tar. The chemical conduct of this hydrocarbon has led to the conclusion that it consists of two benzene residues directly united, as in diphenyl, $C_6H_5-C_6H_5$; and that a further connection between the benzene residues is established through a group $-CH = CH-$, thus giving as the expression of the structure the formula



$$\begin{array}{ccc} C_6H_4 & - & C_6H_4 \\ | & & | \\ CH & = & CH \end{array}.$$

## CHAPTER XXI.

## GLUCOSIDES, ALKALOIDS, ETC.—CONCLUSION.

UNDER the head of the sugars, reference was made (see p. 178) to a class of bodies called *glucosides*, which occur in nature in the vegetable kingdom. These bodies break up under the influence of dilute acids or ferments into sugar and other bodies. Thus, salicin breaks up, according to the equation

$$C_6H_4(OH)CH_2(OC_6H_{11}O_5) + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Salicylic alcohol.}}{C_6H_4(OH)CH_2OH}$$

into dextrose and salicylic alcohol, the alcohol corresponding to salicylic acid. Some of the more important glucosides are mentioned below.

**Aesculin, $C_{15}H_{16}O_9 + 1\frac{1}{2}\,H_2O$,** occurs in the bark of the horse-chestnut tree (*Aesculus Hippocastanum*). It breaks up into dextrose and aesculetin: —

$$\underset{\text{Aesculin.}}{C_{15}H_{16}O_9} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Aesculetin.}}{C_9H_6O_4}.$$

Its water solution shows blue fluorescence.

**Amygdalin, $C_{20}H_{27}NO_{11} + 3\,H_2O$,** occurs particularly in bitter almonds; also, in the kernels of apples, pears, peaches, plums, cherries, etc. With emulsin, which is an aqueous extract of almonds, amygdalin is broken up in benzoic aldehyde, hydrocyanic acid, and dextrose: —

$$C_{20}H_{27}NO_{11} + 2\,H_2O = C_7H_6O + CNH + 2\,C_6H_{12}O_6.$$

**Tannins.** — Under this head are included a large number of substances, some of which are glucosides. They all give either a blue or a green color with ferric salts. They have a bitter, astringent taste; are precipitated by solutions of gelatin; precipitate solutions of metals, and absorb oxygen in alkaline solution. They also unite with animal membranes, forming compounds which resist the putrefactive forces, thus *tanning* them, or converting them into leather. Reference has already been made to gallo-tannic acid, which breaks up into gallic acid and glucose.

**Helicin,** $C_{13}H_{16}O_7 + \frac{3}{4} H_2O$, is formed by the oxidation of salicin (which see). It has also been made artificially by mixing an alcoholic solution of acetochlorhydrose with the potassium compound of salicylic aldehyde: —

$$C_6H_7ClO_5(C_2H_3O)_4 + C_7H_5O_2K + 4\,C_2H_6O$$
$$= C_{13}H_{16}O_7 + KCl + 4\,C_2H_5.C_2H_3O_2.$$

Acetochlorhydrose is formed by heating dextrose with an excess of acetyl chloride.

Helicin breaks up into dextrose and salicylic aldehyde.

**Indican,** $C_{26}H_{31}NO_{17}$, occurs in woad. It yields, among other products, dextrose and indigo blue: —

$$C_{26}H_{31}NO_{17} + 2\,H_2O = 3\,C_6H_{10}O_6 + \underset{\text{Indigo blue.}}{C_8H_5NO}.$$

**Myronic acid,** $C_{10}H_{19}NS_2O_{10}$, is found in the form of the potassium salt in black mustard seed. When treated with myrosin, which is contained in the aqueous extract of white mustard seed, potassium myronate is converted into dextrose, allyl mustard oil, and potassium bisulphate: —

$$C_{10}H_{18}NS_2O_{10}K = C_6H_{12}O_6 + C_3H_5.NCS + KHSO_4.$$

**Salicin,** $C_{13}H_{18}O_7$, occurs in willow bark, and in the bark and leaves of poplars. Its decomposition into salicylic aldehyde and dextrose has been referred to (see preceding page).

**Saponin, $C_{32}H_{54}O_{18}$,** is found in soap root (*Saponaria officinalis*). Its water solution forms a lather like that formed by soap. This property is frequently utilized for the purpose of giving to "soda water" the appearance of effervescence.

## Alkaloids.

The alkaloids are compounds occurring in plants, frequently constituting those parts of the plants which are most active when taken into the animal body. They are hence sometimes called the *active principles* of the plants. Many of these substances are used in medicine. As regards their chemical character, they are basic in the sense that ammonia is basic; they contain nitrogen, and form salts, just as ammonia does, *i.e.*, by direct addition to the acids. These and other facts lead to the belief that the alkaloids are related to ammonia — that they are substituted ammonias. Recently it has been shown that several of the alkaloids are related to pyridine (see p. 307) and quinoline (see p. 343). Only a few of the more important alkaloids need be mentioned here.

### *Alkaloids of Peruvian Bark.*

**Quinine, $C_{20}H_{24}N_2O_2 + 3\,H_2O$.** — This valuable substance is obtained from the outer bark of the Cinchona varieties. When oxidized, it yields derivatives of pyridine. In view of the interest connected with quinine, the discovery of its relation to pyridine and quinoline has led to a large number of investigations on the derivatives of these two bases, and it is probable that before long it will be possible to make quinine synthetically in the laboratory.

The salts of quinine are formed by direct addition of the base to the acids. Thus, we have

| | |
|---|---|
| *Quinine hydrochloride* . | $C_{20}H_{24}N_2O_2 . HCl$; |
| *Quinine nitrate* . . . . | $C_{20}H_{24}N_2O_2 . HNO_3$; |
| *Quinine sulphate* . . . | $C_{20}H_{24}N_2O_2 . H_2SO_4$, etc., etc. |

**Cinchonine**, $C_{19}H_{22}N_2O$, **cinchonidine**, $C_{19}H_{22}N_2O$, and other bases occur with quinine in Peruvian bark.

**Cocaine**, $C_{17}H_{21}NO_4$, is found in cocoa leaves (*Erythroxylon coca*). Very little is known regarding its chemical nature. Its hydrochloric acid salt, $C_{17}H_{21}NO_4 . HCl$, has recently come into prominence in medicine, owing to the fact that a small quantity of its solution placed upon the eye causes insensibility to pain.

**Nicotine**, $C_{10}H_{14}N_2$, occurs in tobacco leaves in combination with malic acid. Potassium permanganate converts it into nicotinic acid, which is one of the possible pyridine-monocarbonic acids.

### *Alkaloids of Opium.*

Opium is the evaporated sap which flows from incisions in the capsules of the white poppy (*Papaver somniferum*), before they are ripe. The two principal alkaloids contained in opium are morphine and narcotine.

**Morphine**, $C_{17}H_{19}NO_3 + H_2O$, is a crystallizable solid which is difficultly soluble in water, alcohol, and ether. When decomposed, it yields pyridine, trimethyl-amine, and phenanthrene, together with other products.

**Narcotine**, $C_{22}H_{23}NO_7$, has been shown to contain three methyl groups, which are split off, as methyl chloride, when the substance is heated with hydrochloric acid.

**Piperine**, $C_{17}H_{19}NO_3$, is contained in black pepper. When treated with alcoholic potash, it breaks up into piperidine and piperic acid: —

$$C_{17}H_{19}NO_3 + H_2O = \underset{\text{Piperidine.}}{C_5H_{11}N} + \underset{\text{Piperic acid.}}{C_{12}H_{10}O_4}.$$

**Piperidine, $C_5H_{11}N$,** which, as just stated, is formed by the decomposition of piperine, has been made synthetically by treating piperidine with nascent hydrogen: —

$$\underset{\text{Pyridine.}}{C_5H_5N} + 6\,H = \underset{\text{Piperidine.}}{C_5H_{11}N}.$$

It may therefore be called *hexa-hydropyridine* (see p. 309).

**Strychnine, $C_{21}H_{22}N_2O_2$, and brucine, $C_{23}H_{26}N_2O_4 + 4\,H_2O$,** are two alkaloids which occur in *nux vomica*.

---

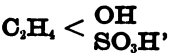
In the animal body occur a large number of complicated substances, the study of which, at this stage, would hardly be profitable. Thus, there are the albumins, caseins, and fibrin; the coloring-matters of the blood, oxyhämaglobin, hämaglobin, etc. It may be said that, notwithstanding the importance of these substances, our knowledge of their chemistry is quite limited.

The study of the composition of animal substances, such as milk, urine, etc., and of the relations of the chemical substances occurring in the body to the processes of life, is the object of *physiological chemistry*. Without a good knowledge of the general chemistry of the compounds of carbon, however, the subjects treated under the head of Physiological Chemistry cannot be understood.

# APPENDIX.

PAGE 165. After ninth line from bottom, insert:—

WE have seen that the sulphonic acids and carbonic acids are analogous; that, for example, methyl-sulphonic acid, $CH_3.SO_3H$, is analogous to methyl-carbonic or acetic acid, $CH_3.CO_2H$. Now, just as the hydroxy-acids above considered are derived from the carbonic acids by the introduction of hydroxyl, so we can imagine a series of hydroxy-acids derived in a similar way from the sulphonic acids. Only one such acid is well known, and it alone need be considered. It is—

**Isethionic acid,**  $C_2H_4 < \begin{matrix} OH \\ SO_3H \end{matrix}$, also known as *hydroxy-ethyl-sulphonic acid.* In composition it is analogous to the hydroxy-propionic acids. It is prepared by passing sulphur trioxide into well-cooled alcohol or ether.

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